Biphasic, Homogeneous, and Heterogeneous Hydrocarbon Conversion Reactions with Novel Aluminum Chloride Based Catalyst Systems

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Für Katharina

und Emil

„Wer immer tut, was er schon kann, bleibt immer das, was er schon ist.“

Henry Ford

Abbreviations

br	broad
BMIM	1-butyl-3-methylimidazolium
Bu	butyl
℃	degree celsius
C	quaternary carbon (for ^{13}C NMR spectroscopy)
Cy	cyclohexyl
d	doublet or day(s)
dd	duplicated doublet
δ	chemical shift (ppm)
DMB	2,3-dimethylbutene(s)
dme	dimethoxyethane
Et	ethyl
EROEI	energy returned on energy invested
g	gram(s)
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
h	hour(s)
HDPE	high density polyethylene
HEX	*n*-hexene(s)
ΔH_m	melting enthalpy
HT-GPC	high temperature gel permeation chromatography
Hz	Hertz
IFP	Institut Français du Pétrole
J	coupling constant (Hz)
K	Kelvin
L	ligand
LPG	liquefied petroleum gas
LLDPE	linear low density polyethylene
LNG	liquefied natural gas
m	meta
m	multiplet
M	molecular weight (for mass spectrometry)
M_n	number average molecular weight
M_w	weight average molecular weight
MAO	methylaluminoxane
Me	methyl
mg	milligram(s)
MHz	Megahertz
min	minute(s)
ml	milliliter
mmol	millimol
MP	2-methylpentene(s)
MPa	megapascal
MS	mass spectrometry
N-MP	N-methylpyrrole
NMR	nuclear magnetic resonance
not. det.	not determined
p	para
PDI	polydispersity index (= M_w / M_n)
PE	polyethylene
Ph	phenyl
R	alkylchain
RON	research octane number
RT	room temperature
s	singlet
SHOP	Shell higher olefin process
SILP	supported ionic liquid phase
t	triplet or time
T	temperature
T_m	melting point
TMA	trimethylaluminum
THF	tetrahydrofurane
wt%	weight percent
X	halide
Ξ	reference frequency (for NMR spectroscopy)

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1 Summary

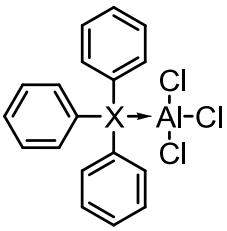
The aim of this thesis was the development of novel cocatalysts for nickel catalyzed olefin dimerization and oligomerization reactions. For this purpose, cheap and air stable Lewis acidic chloroaluminate ionic liquids were the starting point for our investigations. Chloroaluminate melts are immiscible with hydrocarbon phases, and thus, biphasic oligomerization reactions allow a simple product separation by decantation.

a) $[Cation]Cl + 2\ AlCl_3 \longrightarrow [Al_2Cl_7]^-[Cation]^+$

Acidic Ionic Liquid: Uncontrolled Cationic Olefin Oligomerization

b) $[Al_2Cl_7]^- + Buffer \rightleftharpoons [AlCl_4]^- + Cl_3Al{\leftarrow}Buffer$

Buffered Ionic Liquid: activates Ni-Complexes

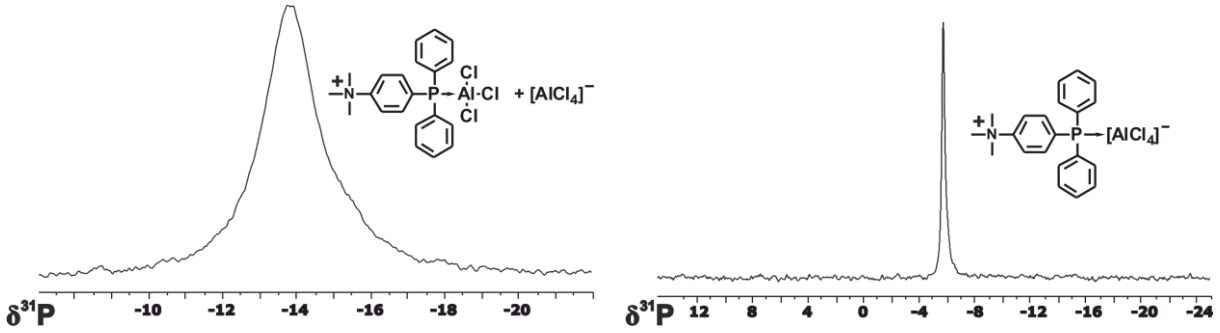
c)  X = N, P, Bi

Scheme 1: Formation of highly Lewis acidic $[Al_2Cl_7]^-$ anions in chloroaluminate ionic liquids (a), their donor-acceptor interaction with a buffer additive (b) and examples for successfully employed buffers (c).

Unmodified chloroaluminate melts containing excess aluminum chloride predominantly catalyze non selective, cationic olefin oligomerization reactions. We found that the addition of triphenylamine, triphenylphosphine, or triphenylbismuth donors efficiently suppressed these side reactions to yield an ideal cheap and air stable ionic liquid cocatalyst for common nickel complexes used for olefin dimerization or oligomerization reactions (**Scheme 1**). Especially triphenylbismuth was able to buffer slightly acidic chloroaluminate melts as well as highly acidic compositions. For nickel catalyzed dimerization reactions, we found that high buffering levels led to very high selectivities to give dimers, while systems with lower buffer contents were less selective but

extremely active. We proposed a mechanism for Ni(II) catalyzed selective olefin dimerization reactions in alkylaluminum free buffered chloroaluminate melts that explained our catalytic results. Further, the melting points of acidic chloroaluminate melts were reduced upon addition of $BiPh_3$. Thus, room temperature ionic liquid compositions derived from 100 different organic halide salts were screened towards their performances in nickel catalyzed selective propene dimerization reactions. An N-methylpyrrolidine hydrochloride based system maintained an excellent performance even after seven catalytic cycles. Amines and $BiPh_3$ used for such systems can be easily recovered by acid base extraction. Subsequently, an optimized composition was successfully employed to dimerize ethene, propene, 1-butene, and 1-hexene with high activities and selectivities. The presence of sterically demanding tricyclohexylphosphine ligands in such systems led to the formation of valuable branched products.

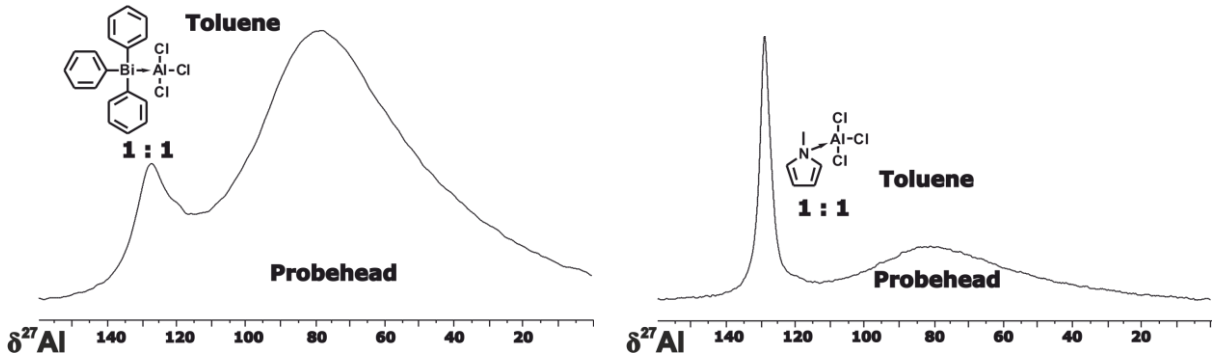
In order to minimize leaching effects and to investigate the interactions of a donor additive with the ionic liquid, a cationic *para*-trimethylammonium substituted triphenylphosphine derivative was synthesized. Its interaction with the ionic liquid was monitored by means of ^{31}P NMR spectroscopy (**Scheme 2**). While strong P–Al interactions in highly Lewis acidic compositions resulted in a broad ^{31}P NMR peak, a weak interaction in neutral chloroaluminate melts was reflected in a sharp ^{31}P NMR signal.



Scheme 2: ^{31}P NMR spectra of the interaction of a cationic triphenylphosphine derivative with a highly Lewis acidic (left) and a neutral chloroaluminate ionic liquid (right).

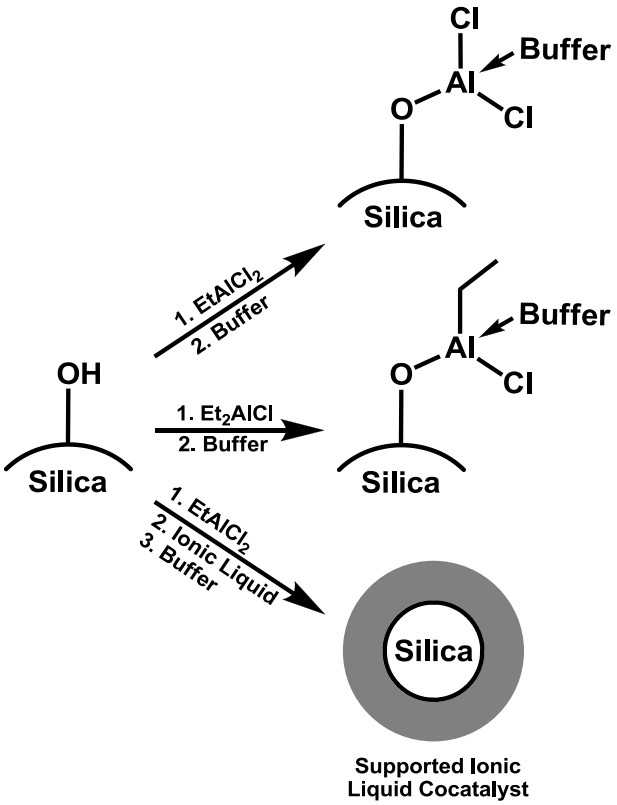
The concept of buffering highly Lewis acidic aluminum chloride centers was also transferred to binary homogeneous systems. In combination with stoichiometric amounts of $BiPh_3$ or N-methylpyrrole buffer, aluminum chloride readily dissolved in toluene and methylene chloride to form a highly efficient, cheap and air stable

cocatalyst for nickel catalyst precursors. The catalytic results of these buffered homogeneous cocatalysts for olefin dimerization reactions were superior to common pyrophoric cocatalysts used for the activation of nickel catalyst precursors like $EtAlCl_2$ or Et_2AlCl. Furthermore, the Lewis acidities of these binary homogeneous cocatalyst solutions could be tuned precisely by the choice of the solvent and the type and amount of buffer. Also, buffer addition efficiently suppressed isomerization reactions of the α-olefinic products. The interaction of $BiPh_3$ and N-methylpyrrole with $AlCl_3$ was monitored by ^{27}Al NMR spectroscopy (**Scheme 3**). Strong interactions resulted in broad ^{27}Al NMR signals and weakly Lewis acidic compositions. In contrast, cocatalyst systems with sharp ^{27}Al NMR signals displayed high Lewis acidities.



Scheme 3: ^{27}Al NMR spectra of the donor-acceptor interaction of $AlCl_3$ with triphenyl-bismuth (left) and N-methylpyrrole (right) in toluene.

Further, the concept of buffering highly Lewis acidic aluminum species was extended to heterogeneous systems (**Scheme 4**). The Lewis acidities of $EtAlCl_2$ or Et_2AlCl modified silicas were reduced by the addition of $BiPh_3$ or N-methylpyrrole buffers. Buffered surface modified silica cocatalysts were successfully employed to activate nickel complexes for highly selective olefin dimerization reactions. Also, surface modified silica proved to be an ideal substrate for the formation of supported ionic liquid phase (SILP) cocatalyst systems used in nickel catalyzed olefin dimerization reactions.



Scheme 4: Silica surface modification to give buffered heterogeneous und supported ionic liquid cocatalysts.

Buffered biphasic, homogeneous, and heterogeneous aluminum based cocatalysts were also able to activate a nickel diimine complex for the polymerization of ethene. The polymer yields, molecular weights and polydispersities (PDI) of the polyethylenes could be influenced by varying the solvent or the type and amount of buffer. Transition metal catalyzed olefin polymerization reactions activated by $AlCl_3$ based cocatalysts have not been reported yet, neither in ionic liquids nor for homogeneous systems.

We developed the first air stable cocatalyst systems solely based on aluminum chloride. The concept of buffering highly Lewis acidic aluminum species to give buffered cocatalysts was successfully applied for biphasic, homogeneous, and heterogeneous olefin dimerization and polymerization reactions with nickel complexes. With the right combination of solvent, type and amount of buffer, and process parameters, tailor-made cocatalysts for numerous catalyst precursors can be designed. The systems proved to be highly active, long term stable and very selective for olefin dimerization or polymerization reactions. Due to the cheap components and the possibility to recycle

buffers or halide salts, these new systems provide promising alternatives to established alkylaluminum based cocatalyst systems.

Highly Lewis acidic chloroaluminate melts were also employed for catalytic cracking and oxidative coupling reactions of saturated hydrocarbons. We found that the presence of molecular oxygen increased the conversions of *n*-heptane to give gaseous cracking products by more than one order of magnitude compared to reactions under inert atmosphere. Cyclic alkanes were efficiently dimerized and trimerized due to oxidative coupling reactions in the presence of O_2, while only skeletal isomerization reactions occurred in argon atmosphere.

Further, it was found that up to stoichiometric amounts of zirconium tetrachloride and hafnium tetrachloride could be dissolved in neutral chloroaluminate melts. From such highly Lewis acidic ternary mixtures, crystals of $[Ti_2Cl_{10}][BMIM]_2$, $[Zr_2Cl_{10}][BMIM]_2$ (BMIM = 1-butyl-3-methylimidazolium), and $[Hf_2Cl_9][PhNMe_3]$ were obtained, and their crystal structures were determined.

Zusammenfassung

Das Ziel der vorliegenden Arbeit war die Entwicklung neuartiger Cokatalysatoren für nickelhaltige Katalysatorvorstufen zur Dimerisierung und Oligomerisierung von Olefinen. Als Ausgangskomponenten dienten billige und luftstabile Lewis-saure ionische Flüssigkeiten auf der Basis von Chloroaluminatschmelzen. Diese mischen sich nicht mit Kohlenwasserstoffen, wodurch in zweiphasigen Oligomerisierungsreaktionen eine einfache Produktabtrennung durch Dekantieren ermöglicht wird.

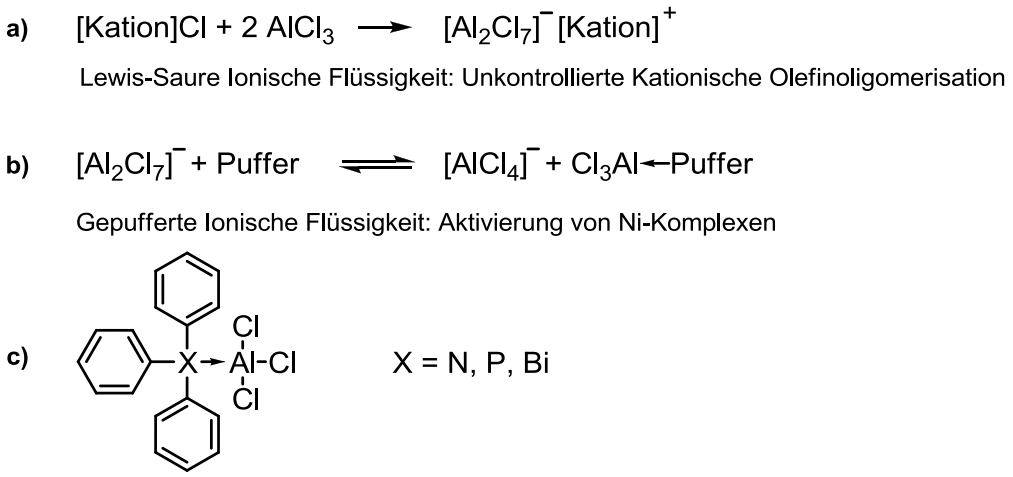


Abbildung 1: Bildung von stark Lewis-sauren $[Al_2Cl_7]^-$-Anionen in Chloroaluminatschmelzen (a), deren Donor-Akzeptor-Wechselwirkung mit einem Puffer-Additiv (b) und Beispiele für erfolgreich eingesetzte Puffer-Additive (c).

Reine Chloroaluminatschmelzen, in denen ein Überschuss an Aluminiumchlorid vorliegt, katalysieren in erster Linie die unselektive, kationische Oligomerisation von Olefinen. Wir haben festgestellt, dass solche Nebenreaktionen durch die Zugabe von Triphenylamin-, Triphenylphosphin- oder Triphenylbismut-Donoren wirkungsvoll unterdrückt werden können. Die resultierenden ionischen Flüssigkeiten erwiesen sich als sehr gute, billige und luftstabile Cokatalysatoren zur Aktivierung von Nickelkomplexen, die standardmäßig für Olefin-Dimerisierungs- und Oligomerisierungsreaktionen verwendet werden (**Abbildung 1**). Durch die Zugabe von Triphenylbismut konnte die Lewis-

Acidität sowohl von schwach sauren als auch von stark sauren Chloroaluminatschmelzen besonders gut reguliert werden. Bei Dimerisierungsreaktionen mit Nickelkomplexen zeigte sich, dass die Zugabe großer Mengen von Triphenylbismut die Dimerselektivität stark begünstigte. Im Gegensatz dazu führten geringe $BiPh_3$-Konzentrationen dazu, dass die entsprechenden Katalysatorsysteme weniger selektiv, dafür aber extrem aktiv waren. Wir haben einen Mechanismus für selektive Dimerisierungsreaktionen von Olefinen mit Ni(II)-Komplexen in Chloroaluminatschmelzen vorgeschlagen, in denen keine Alkylaluminiumverbindungen vorhanden sind. Der Mechanismus erklärt die von uns erhaltenen experimentellen Resultate für Donor-modifizierte („gepufferte“) Lewis-saure ionische Flüssigkeiten. Durch die Schmelzpunktserniedrigung saurer Chloroaluminatschmelzen bei Zugabe von Triphenylbismut konnten in einer groß angelegten Testreihe ionische Flüssigkeiten aus hundert verschiedenen organischen Halogenidsalzen hergestellt und für die selektive Dimerisierungsreaktion von Propen mit Nickelkomplexen getestet werden. Ein System, das auf N-Methylpyrrolidin Hydrochlorid basierte, zeigte auch nach sieben aufeinanderfolgenden Experimenten eine hervorragende Dimerselektivität. Die verwendeten Amine und $BiPh_3$ können problemlos durch Säure-Base-Extraktion zurückgewonnen werden. Ein optimiertes System erwies sich anschließend als hochaktiv und hochselektiv bei der Dimerisierung von Ethen, Propen, 1-Buten und 1-Hexen mit Nickelkomplexen. Bei Anwesenheit sterisch anspruchsvoller Tricyclohexylphosphin-Liganden bildeten sich vermehrt hochwertige, stark verzweigte Produkte.

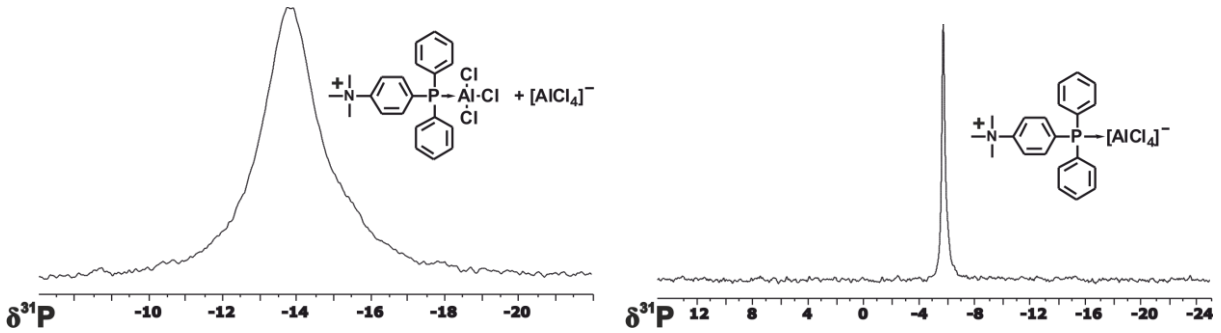


Abbildung 2: ^{31}P-NMR-Spektren der Wechselwirkung eines kationischen Triphenylphosphin-Derivates mit einer stark Lewis-sauren (links) und einer neutralen Chloroaluminatschmelze (rechts).

Um ein Auswaschen zu verhindern und die Wechselwirkung eines Donor-Additivs mit Chloroaluminatschmelzen untersuchen zu können, wurde ein kationisches Triphenylphosphin-Derivat hergestellt. Dessen Wechselwirkung mit der ionischen Flüssigkeit wurde mit Hilfe der ^{31}P-NMR-Spektroskopie untersucht (**Abbildung 2**). Stark Lewis-saure Zusammensetzungen führten zu einer starken P–Al-Wechselwirkung und breiten ^{31}P-NMR-Signalen, während scharfe ^{31}P-NMR-Signale in neutralen ionischen Flüssigkeiten auf eine geringe Wechselwirkung hindeuteten.

Das Konzept der Donor-Akzeptor-Wechselwirkung mit stark Lewis-sauren Aluminiumzentren konnte auch auf binäre, homogene Systeme erweitert werden. Bei Zugabe stöchiometrischer Mengen an $BiPh_3$ oder N-Methylpyrrol löste sich Aluminiumchlorid in Toluol oder Dichlormethan. Mit der so erhaltenen, luftstabilen und preisgünstigen Lösung konnten erfolgreich Nickelkomplexe aktiviert werden, die daraufhin die hochselektive Dimerisierung von α-Olefinen katalysierten. Die dabei erzielten Ergebnisse waren besser als die Resultate mit den standardmäßig für Nickelkomplexe verwendeten, pyrophoren Cokatalysatoren $EtAlCl_2$ oder Et_2AlCl.

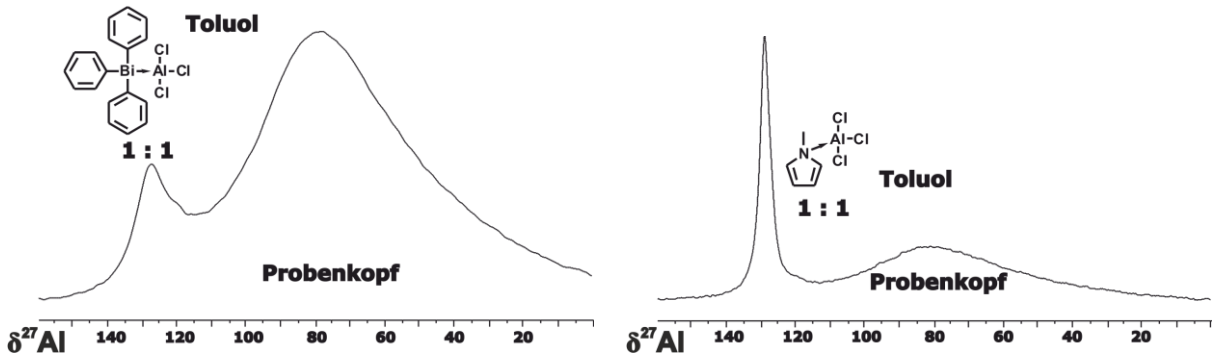


Abbildung 3: ^{27}Al-NMR-Spektren der Donor-Akzeptor-Wechselwirkung von $AlCl_3$ mit Triphenylbismut (links) und N-Methylpyrrol (rechts) in Toluol.

Darüber hinaus konnte die Lewis-Acidität dieser homogenen Zweikomponenten-Cokatalysatorlösung durch die Wahl des Lösungsmittels und der Art und des Überschusses an Donor-Komponenten äußerst genau eingestellt werden. Zudem wurde durch Pufferzugabe die Isomerisierung der gebildeten Primärprodukte wirkungsvoll unterdrückt, was zur Bildung hoher Anteile an α-Olefinen führte. Die Wechselwirkung zwischen $AlCl_3$ und $BiPh_3$ oder N-Methylpyrrol wurde mit Hilfe der ^{27}Al-NMR-Spektro-

skopie genauer untersucht (**Abbildung 3**). Starke Wechselwirkungen ergaben breite ^{27}Al-NMR-Signale und gleichzeitig schwach Lewis-saure Lösungen. Im Gegensatz dazu wiesen Systeme mit scharfen ^{27}Al-NMR-Signalen eine starke Lewis-Acidität auf.

Das Konzept der Wechselwirkung von Donor-Molekülen mit stark Lewis-sauren Aluminiumzentren konnte auch auf heterogene Systeme übertragen werden (**Abbildung 4**). Die Lewis-Acidität von Silica, dessen Oberfläche mit $EtAlCl_2$ oder Et_2AlCl modifiziert wurde, konnte durch die Zugabe von $BiPh_3$ oder N-Methylpyrrol als Donor-Additive reguliert werden. Solches Donor-modifiziertes Silica wurde erfolgreich zur Aktivierung von Nickelkomplexen für hochselektive Dimerisierungsreaktionen von α-Olefinen verwendet. Oberflächenmodifiziertes Silica erwies sich zudem als gut geeignetes Trägermaterial für die Herstellung von gepufferten Cokatalysatoren bestehend aus geträgerten ionischen Flüssigkeiten (SILP).

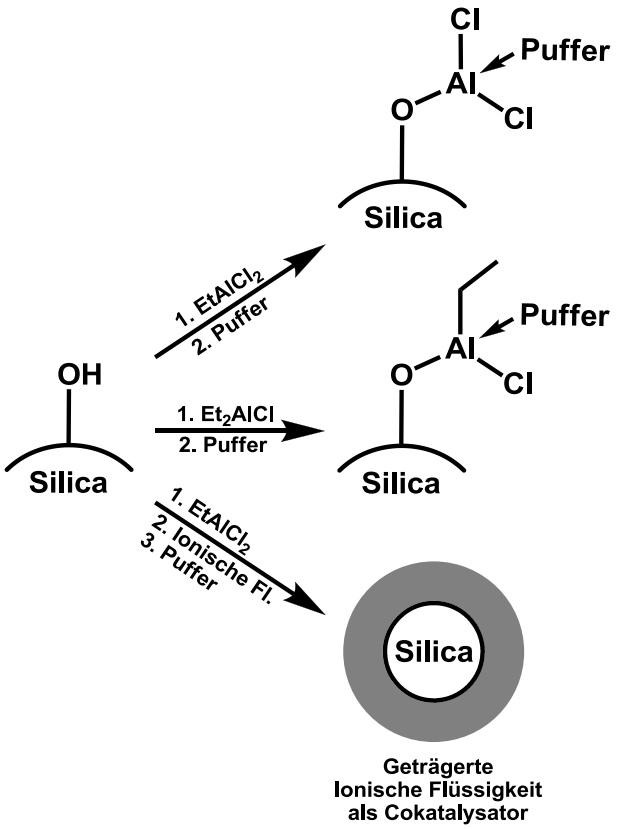


Abbildung 4: Oberflächenmodifizierung von Silica zur Herstellung von gepufferten heterogenen Cokatalysatoren und geträgerten ionischen Flüssigkeiten.

Mit gepufferten Aluminium-Cokatalysatoren konnte überdies ein Nickeldiimin-Komplex für die homogene, heterogene oder zweiphasige Polymerisation von Ethen aktiviert

werden. Die Polymerausbeute, das Molekulargewicht und der Polydispersitätsindex (PDI) des so erzeugten Polyethylens konnte durch die Wahl des Lösungsmittels und der Art und der Menge des zugegebenen Donor-Additivs beeinflusst werden. Die Olefinpolymerisation mit Übergangsmetallkomplexen wurde bisher noch nicht mit auf $AlCl_3$ basierenden Cokatalysatoren beschrieben, weder in homogenen Systemen noch in ionischen Flüssigkeiten.

Im Rahmen dieser Arbeit wurden die ersten luftstabilen Aluminium-Cokatalysatorsysteme entwickelt, die ausschließlich auf $AlCl_3$ basieren. Das Konzept der Donor-Akzeptor-Wechselwirkung von stark Lewis-sauren Aluminiumzentren mit schwach Lewis-basischen Donor-Molekülen konnte erfolgreich auf zweiphasige, homogene und heterogene Systeme angewendet werden. Die erhaltenen Mischungen erwiesen sich als effiziente Cokatalysatoren für die selektive Dimerisierung und Polymerisation von Olefinen mit Nickelkomplexen. Durch eine geeignete Kombination des Lösungsmittels, der Art und der Menge der Donor-Komponente und der Prozessparameter können so maßgeschneiderte Cokatalysatoren für eine Vielzahl von Katalysatorvorstufen erzeugt werden. Die getesteten Systeme erwiesen sich bei der Olefin-Dimerisierung und Polymerisation als äußerst aktiv, langzeitstabil und sehr selektiv. Durch die Verwendung von preisgünstigen Komponenten und der Möglichkeit, Donor-Additive oder Halogenidsalze zurückzugewinnen, stellen derartige Systeme vielversprechende Alternativen zu den standardmäßig verwendeten Alkylaluminium-Cokatalysatoren dar.

Stark Lewis-saure Chloroaluminatschmelzen wurden weiterhin für Cracking- und Kupplungsreaktionen gesättigter Alkane verwendet. Beim Cracking von *n*-Heptan in Gegenwart von molekularem Sauerstoff erhöhte sich der Umsatz um mehr als eine Größenordnung im Vergleich zu Reaktionen unter Schutzgas. Dabei fielen vor allem gasförmige Alkane als Reaktionsprodukte an. Dagegen führte die gleiche Reaktion mit Cycloalkanen zu oxidativen Kupplungsreaktionen und damit zur Bildung von Dimeren und Trimeren. In Abwesenheit von O_2 bildeten sich hingegen nur Skelettisomere.

Außerdem wurde festgestellt, dass sich bis zu äquimolare Mengen an Zirkoniumtetrachlorid und Hafniumtetrachlorid in neutralen Chloroaluminatschmelzen lösten. Die daraus resultierenden ternären Mischungen waren stark Lewis-sauer. Die Verbindungen $[Ti_2Cl_{10}][BMIM]_2$, $[Zr_2Cl_{10}][BMIM]_2$ (BMIM = 1-butyl-3-methylimidazolium) und $[Hf_2Cl_9][PhNMe_3]$ konnten so kristallisiert und deren Kristallstrukturen bestimmt werden.

2 Introduction

2.1 Fossil Fuels and Oil Refining

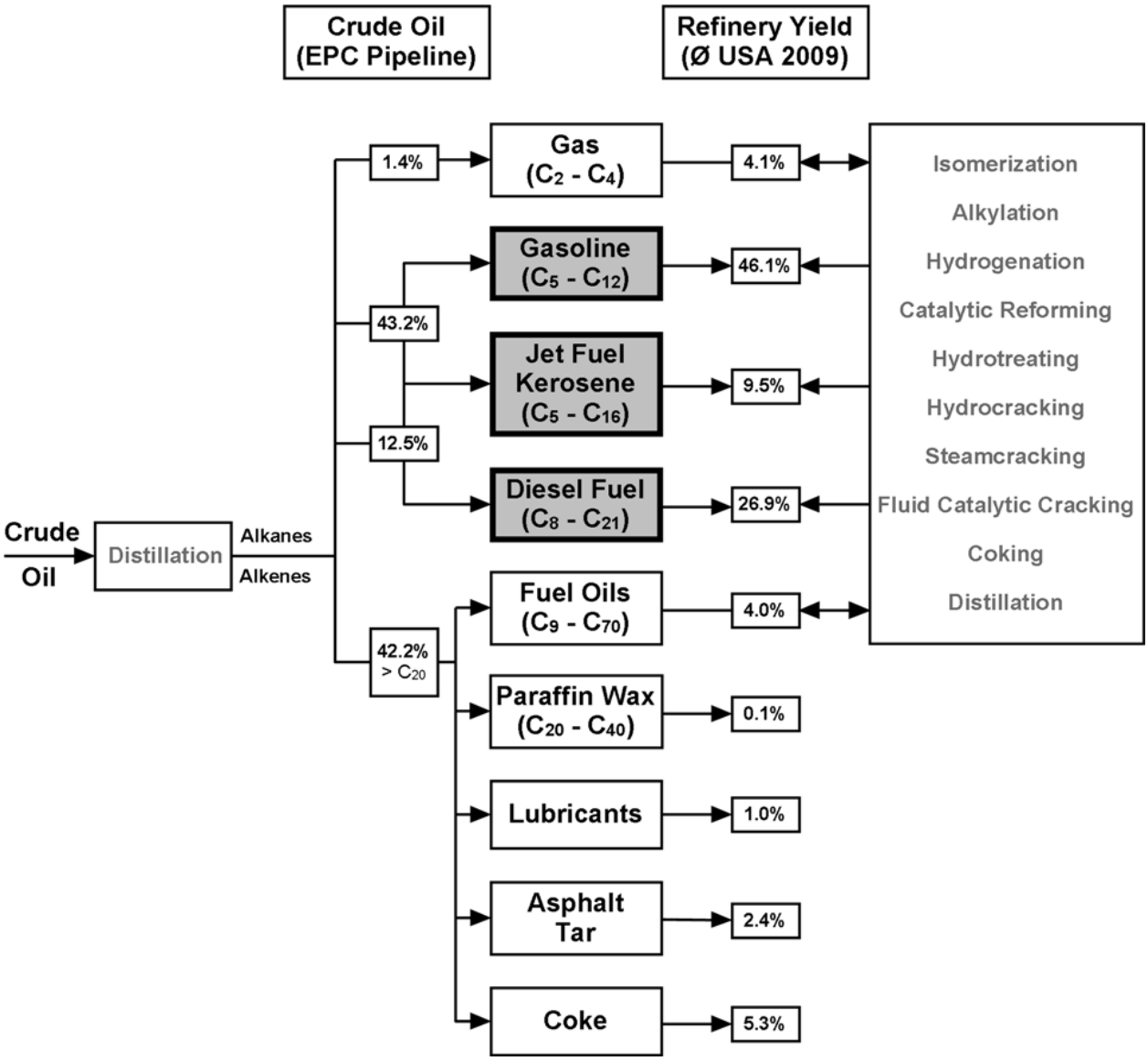
Although renewable energy sources are just beginning to attract attention as serious alternatives, fossil fuels will still be the main source of energy in the next decades. With about 35% in 2009, oil remains the leading fuel followed by coal and natural gas.[1] Besides its use to generate heat or electricity, oil is an indispensable feedstock for the production of fuel oils, gasoline, petrochemicals, or plastic materials.

However, with increasing demand and decreasing resources, oil production becomes more and more energy-intensive. EROEI (energy returned on energy invested) is the amount of usable energy gained from a certain energy resource divided by the energy, which had to be expended. In the beginning, giant oil fields close to the surface were exploited, with negligible energy expenditure. Due to an increasing demand and the high price of oil, even deepwater drilling, tar sands and oil shales have become economic today. However, the net energy gain from these resources is very low compared to conventional oil fields (**Table 1**).

Table 1: Energy returned on energy invested (EROEI) ratios of some fossil fuels.[2]

Fossil Fuel	EROEI
Oil (1940 – 1960)	100
Coal	50
Oil (1970 – 1980)	25
Oil (global average)	19
Natural Gas	10
Tar Sands	5.2 – 5.8
Oil Shale	1.5 – 4

Therefore, it is necessary to increase the efficiency of oil refining processes to maximize the yield of valuable products in combination with a minimum of waste production and energy consumption. Certainly, liquid fuels like gasoline, diesel fuel, or kerosene are the most valuable and useful refinery products since they are the prerequisite for our mobility. Thus, the aim of a typical oil refinery is to maximize the yield of these products, namely the hydrocarbon fraction containing between six and 20 carbon atoms. **Scheme 1** shows the processes and yields of a typical oil refinery.

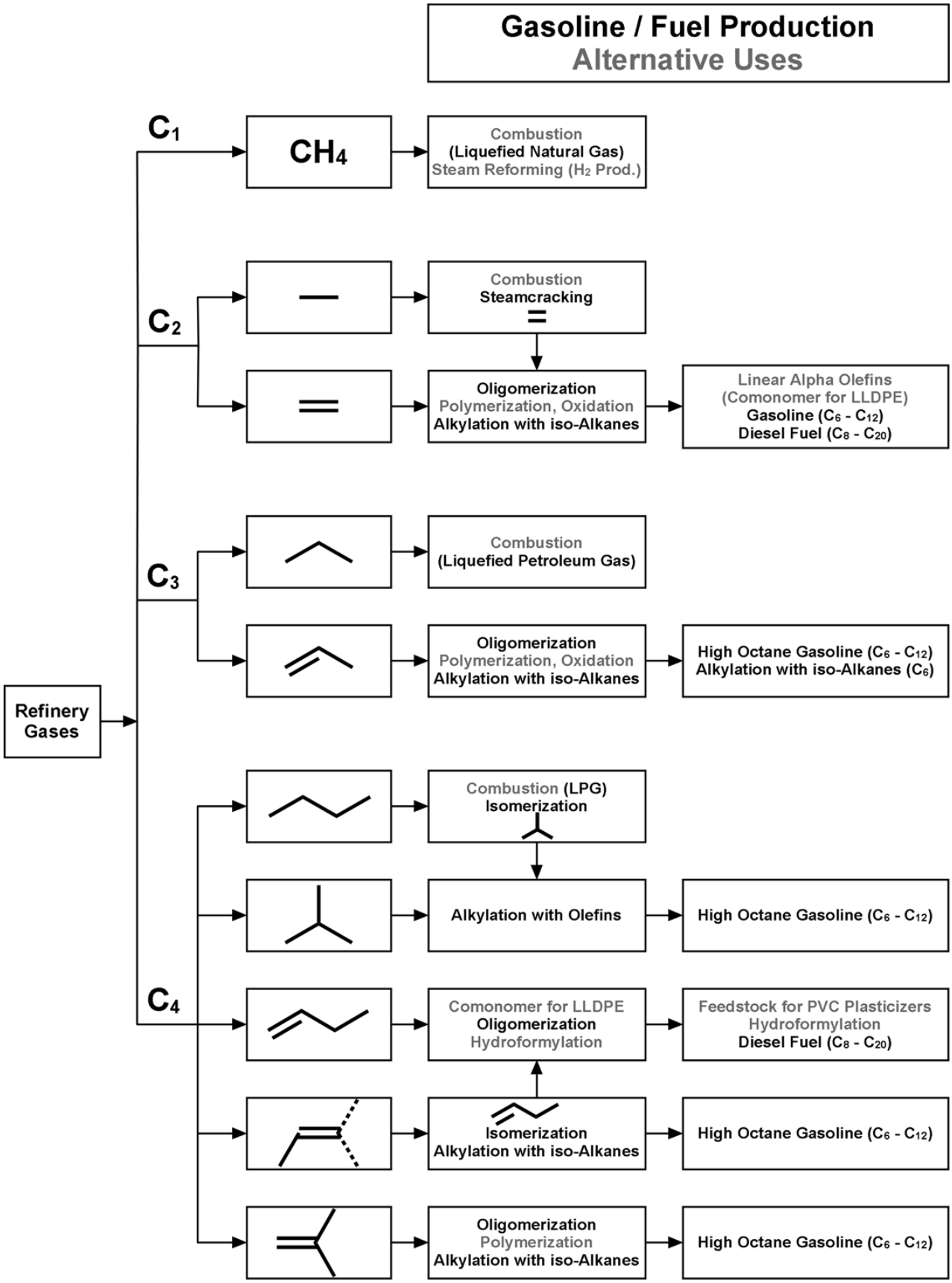


Scheme 1: Simplified crude oil processing in refineries (averaged crude oil compositions of an oil carrying pipeline[3] and averaged output of US refineries in 2009[4]).

First, the crude oil is distilled to yield about 50% of hydrocarbons within the gasoline or diesel range. Subsequently, the gases are transformed to higher hydrocarbons, while the heavy oils are cracked to further increase the gasoline and diesel yield.

Catalytic cracking reactions of high molecular weight hydrocarbons are usually performed at high temperatures and produce more valuable saturated or unsaturated gases or gasoline. Thus, large amounts of C_1 to C_4 alkanes and olefins are produced in refineries in addition to the gaseous fractions dissolved in crude oil. Further, the exploitation of tar sands and oil shales requires an extensive use of catalytic cracking reactions leading to the formation of even more light hydrocarbons. Unlike liquid fuels, gases cannot be stored or transported easily, and consequently, they have to be processed directly in or close to a refinery.

Scheme 2 shows the gases with one to four carbon atoms, which are mainly produced in refineries, and their potential uses. Although α-olefins like ethene, propene, or 1-butene are used as monomers for the production of poly-α-olefins, the market demand for fuels is by far larger than the size of the polymer market. Consequently, oil refining companies are interested in converting these unsaturated gaseous olefins to gasoline or diesel fuels. Besides the alkylation of olefins with isoalkanes catalyzed by anhydrous HF or H_2SO_4, selective dimerization and oligomerization reactions of α-olefins are a promising attempt to achieve that goal.



Scheme 2: Gaseous C_1 – C_4 hydrocarbons accruing in oil refineries and their possible uses.

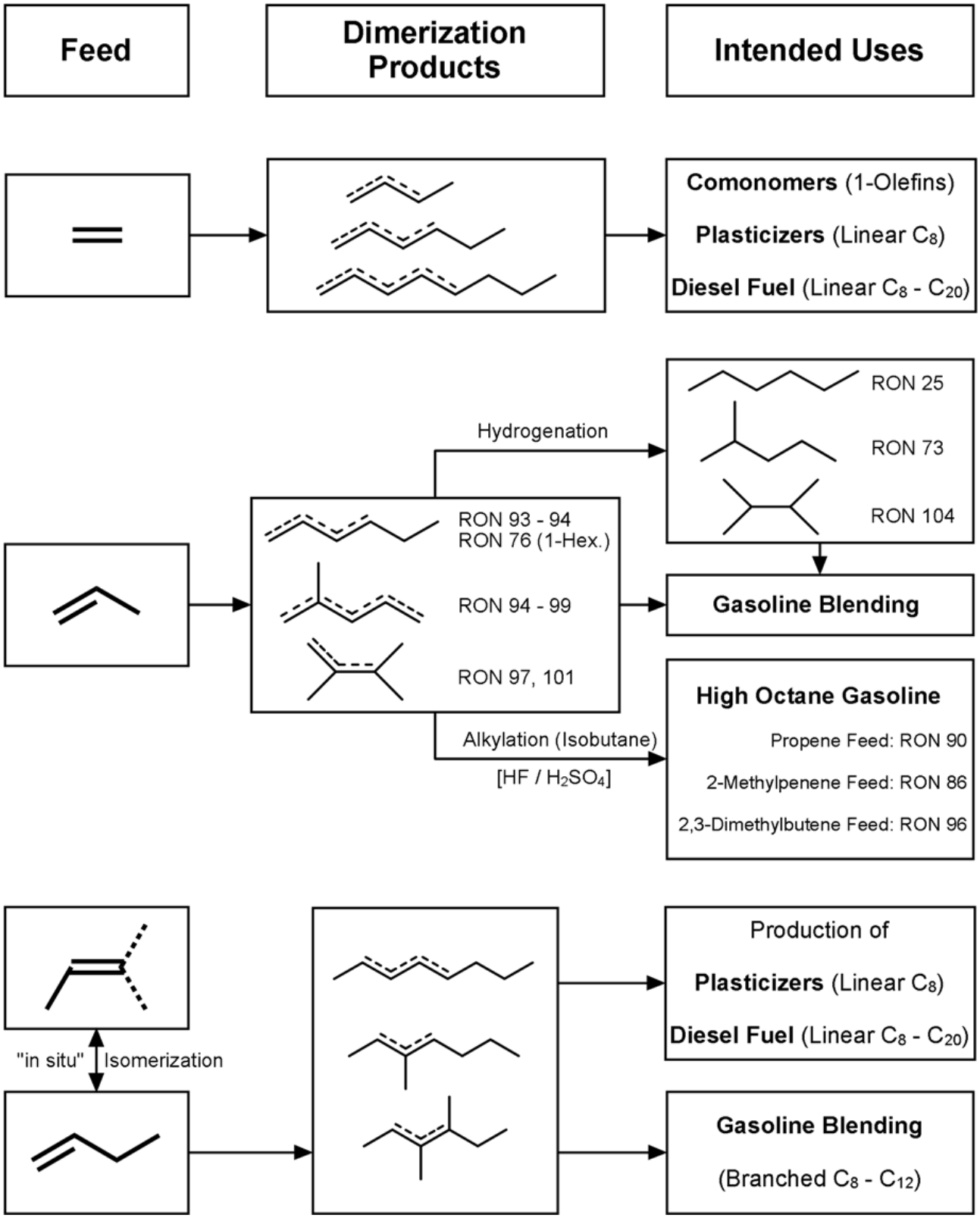
2.2 Dimerization of Short Chain Olefins

The aim of this work was to convert the gaseous olefins ethene, propene, and butenes to products containing six to 20 carbon atoms by selective dimerization and oligomerization reactions. **Scheme 3** provides an overview over the corresponding dimerization and oligomerization products and their intended uses. Initially, the work should be focussed on selective propene dimerization reactions to give gasoline fuels or to upgrade C_3 feeds to yield branched C_6 olefins for the HF catalyzed alkylation with isobutane. For example, selective propene dimerization reactions yield a mixture of *n*-hexenes, 2-methylpentenes, and 2,3-dimethylbutenes. The degree of branching in nickel catalyzed dimerization reactions can be increased by the addition of sterically demanding phosphine ligands like tricyclohexylphosphine.[5] For gasoline, a high degree of branching is desirable. The research octane number (RON) is a measure for the anti-knocking capacity of a fuel. With a higher degree of branching, the RON increases. **Table 2** shows the RONs of typical gasolines.

Table 2: Research octane numbers (RONs) of common gasolines and additives.[6]

Fuel	RON
US Gasoline	85 – 91
Normalbenzin	91
Super Benzin	95
SuperPlus Benzin	98
LPG[1]	103 – 111
LNG[2]	120 – 130
n-Heptane	0
Isooctane	100
Benzene	101
Toluene	110
Xylenes	117

[1] Liquefied petroleum gas. [2] Liquefied natural gas.



Scheme 3: Possible dimerization and oligomerization products of ethene, propene (RONs taken from the literature[7]), and butenes and their intended uses in refineries.

Gasoline with a high RON is necessary to maximize the engine efficiency of modern cars, which is proportional to the compression. With higher compression levels, the tendency of the fuel to self-ignite has to be reduced. Thus, the demand for high octane gasoline is steadily increasing. Especially 2,3-dimethylbutenes display very high research octane numbers around 100. With a boiling point of over 50°C, they can be used directly or after hydrogenation to boost octane ratings even in summer. Further, if the content of high octane aromatics like benzene, toluene, or xylenes will be further restricted by new regulations, appropriate alternatives have to be found. If the C_6 olefins produced by selective propene dimerization reactions are alkylated with isobutane in existing HF alkylation units, even higher boiling, high octane saturated C_{10} gasoline blends could be obtained.[7d]

In contrast to propene, oligomerization reactions of ethene should yield linear olefins. While linear α-olefins are used as co-monomers for the production of LLDPE (linear low density polyethylene), C_8 to C_{20} oligomers can be blended into diesel fuel. For diesel fuels, a low degree of branching is advantageous to favour the self-ignition in the engine. Linear butene dimerization products can also be employed as diesel fuel or feedstock for the production of plasticizers. If branched products are obtained, these can as well be used to blend into gasoline. Ideally, a catalytic system would be able to isomerize and dimerize butenes. The less reactive, thermodynamically more stable 2-butenes are isomerized “in situ” to give the more reactive 1-butene in small amounts, which is subsequently dimerized. In general, internal olefins are of lower value compared to α-olefins, which makes the latter a more economic feedstock for dimerization reactions.

The large number of industrial processes dealing with olefin dimerization and oligomerization mirrors the economic importance of these reactions (**Table 3**). Also, the capacities are enormous. For example, the combined refinery capacities of all IFP (Institut Français du Pétrole) processes listed in **Table 3** exceeded 3.6 million tons per year in 2007.**[8]** The most common transition metals applied for this type of catalysis are group IV metals, nickel, and chromium. While some processes selectively dimerize (Alphabutol®, DIMERSOL®, DIFASOL®) or trimerize (ChevronPhillips) α-olefins, others yield a broad distribution of oligomers. To some extent, the maximum of the oligomer distribution can be influenced by varying process parameters in unselective oligomerization processes. Except the Shell higher olefin process (SHOP), all catalytic

systems require the addition of a cocatalyst. However, the SHOP is operated under more drastic conditions (80 – 140°C, 7 – 14 MPa) compared to nickel systems activated with aluminum based cocatalysts.[9]

Table 3: Industrial transition metal catalyzed oligomerization processes.[8a]

Process	Metal	Cocatalyst	Products
Alphabutol® (IFP)	Ti	$AlEt_3$	1-Butene
DIMERSOL® (IFP)	Ni	$EtAlCl_2$	C_6 / C_8
DIFASOL® (IFP)	Ni	$EtAlCl_2/AlCl_3$ (Ionic Liquid)	C_6 / C_8
SHOP (Shell)	Ni	None (Biphasic)	1-Olefins (C_4 – C_{30})
ChevronPhillips	Cr	Et_xAlCl_{3-x}	1-Hexene
Idemitsu	Zr	Et_xAlCl_{3-x}	1-Olefins (C_6 – C_{30})
Alphaselect® (IFP)	Zr	Et_xAlCl_{3-x}	1-Olefins (C_4 – C_{10})
α-SabLin® (Sabic)	Zr	Et_xAlCl_{3-x}	1-Olefins (variable)
Linear-1® (UOP)	Ni	$NaBH_4$ (Biphasic)	1-Olefins (C_4 – C_{10})

Since nickel compounds are catalytically versatile, cheap and usually insensitive to air or moisture compared to group IV metals, we decided to focus on nickel based dimerization and oligomerization systems. The requirements of a catalytic dimerization system to be developed are as follows. First, the system has to be cheap to compete with established technologies. This requires high activities, lifetimes, conversions and selectivities to both dimer formation and a specific degree of branching. The tolerance towards impurities, mainly oxygen, sulfur, amines, or traces of water, would further reduce the costs of substrate purification. Also, the possibility to recycle or to regenerate spent catalysts would be desirable.

2.3 Cocatalysts for Transition Metal Catalyzed Olefin Dimerization and Polymerization Reactions

Nickel based catalysts usually have to be activated by aluminum alkyls. Common cocatalysts are methylaluminoxane (MAO) and its derivatives, ethylaluminum dichloride, diethylaluminum chloride, triethylaluminum, trimethylaluminum, or mixtures thereof. In **Table 4**, the most common cocatalysts for transition metal catalyzed olefin dimerization and polymerization reactions are listed.[5c, 10] In order to obtain a rough overview over the cost dimensions of these activators, the prices for one mol of cocatalyst were calculated from the cheapest price per unit given by common commercial laboratory chemical suppliers. Of course, the price structure may be completely different for large scale applications. However, the order of magnitude can be estimated.

Perfluorinated organoboron cocatalysts, which are mainly applied for the activation of metallocene complexes,[10u, 10v] are extremely expensive. Although they are only used in stoichiometric amounts, their prices prevent their use for low cost dimerization catalysts. The most common aluminum cocatalyst, MAO, is also the most expensive one. The difficult synthesis und subsequently the high price of MAO is certainly also responsible for the fact that group IV metallocene based systems still have a niche existence. Although other alkylaluminum cocatalysts are less expensive than MAO, the perfect cocatalyst would be $AlCl_3$. Aluminum chloride is among the cheapest chemicals available.

Unfortunately, $AlCl_3$ is insoluble in hydrocarbon solvents[11] and catalyzes side reactions like isomerization, cracking, disproportionation of alkanes as well as alkylation of aromatics with olefins and cationic oligomerization of alkenes.[4, 12] Furthermore, the proposed mechanism based on the insertion of monomers into Ni–H or Ni–C bonds of nickel(II) complexes requires an alkylating agent. Alkylaluminum compounds are pyrophoric and highly sensitive to water, oxygen, or polar impurities. Thus, they are mostly the cost determining factor for commercial applications. Feed streams have to be purified thoroughly prior to the reaction, and the high reactivity requires a cautious handling. Finally, the cocatalyst is destroyed upon product separation of the homogeneous reactions.[13]

Table 4: Common cocatalysts for transition metal catalyzed olefin dimerization and polymerization reactions and their prices for one mol from laboratory chemical suppliers.

Cocatalyst	1 Mol (€)[1]	Supplier	Article	Price (€)[2]
$[Ph_3C][B(C_6F_5)_4]$	73050	ABCR	5 g, 98%	396.00
$B(C_6F_5)_3$	55600	Aldrich	5 g, 95%	543.00
MAO	654	Aldrich	800 ml, 10 wt% (Toluene)	803.00
TIBA	138	Aldrich	500 g	348.50
$EtAlCl_2$	106	Aldrich	800 g, 25 wt% (Toluene)	167.00
$AlMe_3$	82	Aldrich	8 l, 2 M (Toluene)	1310.00
$AlEt_3$	60	Aldrich	1 kg, > 93%	522.00
Et_2AlCl	55	Aldrich	1 kg, > 97%	453.00
$AlCl_3$	3	Aldrich	1 kg, > 98%	22.90

[1] Calculated prices for 1 mol. [2] Articles with the cheapest price per mol were chosen (12/2010).

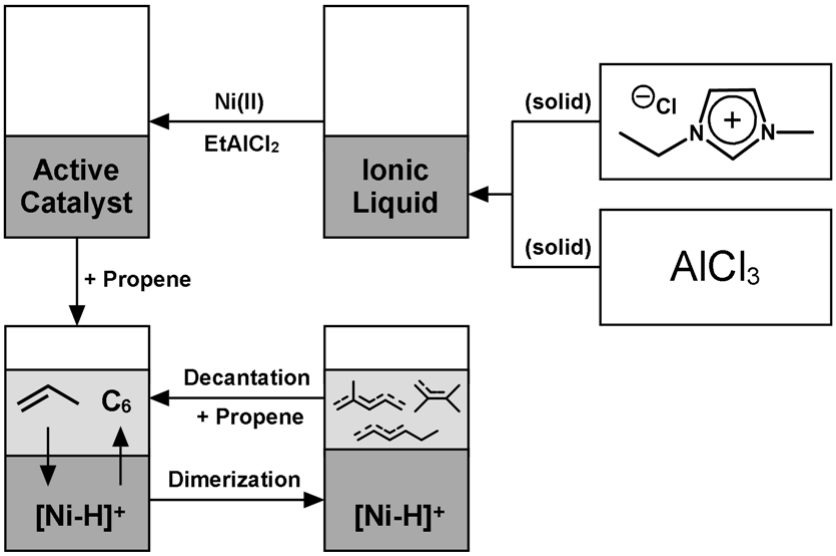
Due to the obvious advantages of $AlCl_3$ in terms of costs and handling, the aim of this work was to find nickel catalyzed dimerization systems, which can be activated by cocatalysts based on aluminum chloride or cheap, aluminum based activators.

Ionic liquids synthesized from $AlCl_3$ are an elegant attempt to overcome the recycling and solubility restrictions of systems based solely on $AlCl_3$.[11, 14] In combination with certain organic cations, $AlCl_3$ forms liquids at ambient temperature over a wide range of compositions, which are immiscible with hydrocarbon phases. The Lewis acidities of such chloroaluminate ionic liquids can be adjusted from basic over neutral to acidic simply by varying the $AlCl_3$ / halide salt ratio.[15] However, basic or neutral liquids do not activate nickel catalysts, while acidic compositions predominantly catalyze uncontrolled cationic olefin oligomerization reactions to yield viscous mixtures of higher oligomers.[12b, 16]

One possibility to suppress such side reactions is the addition of $EtAlCl_2$ to slightly acidic chloroaluminate melts. These $EtAlCl_2$ buffered melts are able to activate nickel

catalyst precursors for selective dimerization reactions of α-olefins.[17] The IFP commercialized this biphasic dimerization process under the trademark DIFASOL®.

Scheme 4 shows the principles of biphasic nickel catalyzed olefin dimerization reactions with chloroaluminate ionic liquids. The nickel catalyst and most of the alkylaluminum species remain within the ionic liquid phase, while the product phase can simply be decanted. Thus, the nickel and aluminum consumption is greatly reduced. DIFASOL® shows higher selectivities to give dimers and can be operated with streams containing smaller amounts of olefins compared to its homogeneous DIMERSOL® analogue.[13, 18] In combination with a much smaller reactor size, this leads to greatly improved process economics.[8a, 8c]



Scheme 4: Synthesis of 1-ethyl-3-methylimidazolium ethylchloroaluminate ionic liquids and their use for biphasic nickel catalyzed propene dimerization reactions.

Due to the obvious advantages of chloroaluminate ionic liquid dimerization systems, which combine facile product decantation and cheap components, the goal was the development of novel, cheap and insensitive chloroaluminate ionic liquid dimerization systems. Furthermore, new homogeneous and heterogeneous cocatalysts based on aluminum chloride or cheap aluminum compounds had to be developed.

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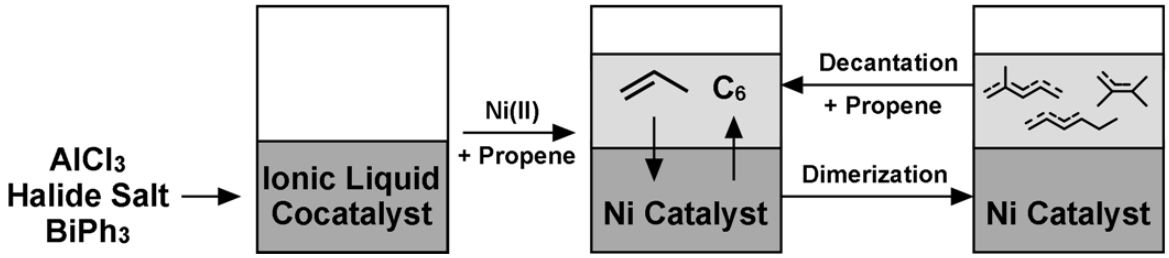
3 Overview of Thesis Results

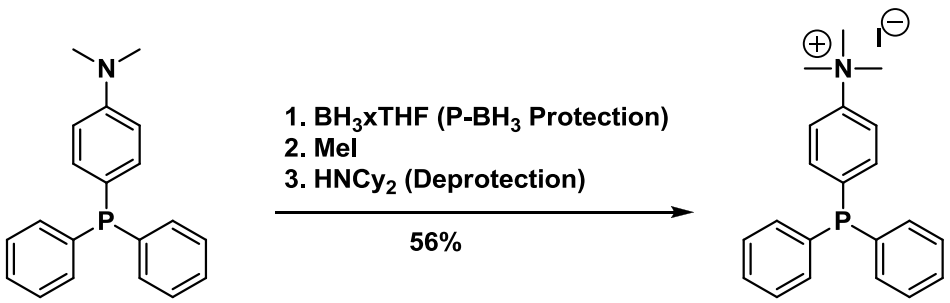
This thesis comprises seven publications, which are presented in chapters 4 – 10.

3.1 Heavy Metal with Heavy Impact: Olefin Dimerization Reactions in Triphenylbismuth Buffered Chloroaluminate Ionic Liquids



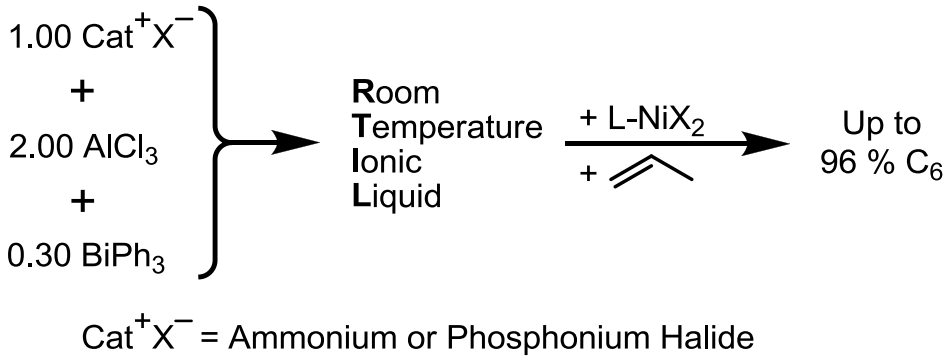
The addition of weak Lewis bases such as NPh_3, PPh_3, or $BiPh_3$ to Lewis acidic chloroaluminate ionic liquids yielded efficient cocatalysts for nickel catalyst precursors in highly selective biphasic dimerization reactions of α-olefins. Triphenylbismuth buffered systems were found to produce up to 96% dimers from propene. Selectivities and activities were influenced by varying the compositions of the ionic liquids. Further, buffer addition reduced the melting points of the resulting liquids. This effect allowed a screening of many different organic halide salts, which were found to strongly influence lifetimes and selectivities of the corresponding biphasic olefin dimerization systems. An optimized N-methylpyrrolidine hydrochloride based system dimerized ethene, propene, 1-butene, and 1-hexene with high selectivities. It is even possible to recycle amines and buffers used for these compositions by a simple acid base extraction of spent ionic liquid catalyst systems. We also proposed a mechanism for these Ni(II) catalyzed selective olefin dimerization reactions in alkylaluminum free buffered chloroaluminate melts. The addition of small amounts of $BiPh_3$ to an ionic liquid composition used in the commercial DIFASOL® process increased the selectivity to give dimers from a biphasic propene dimerization reaction by 15%.

3.2 Facile Synthesis of new Cationic Triphenylphosphine Derivatives and their Use for Propene Dimerization Reactions in Buffered Chloroaluminate Ionic Liquids



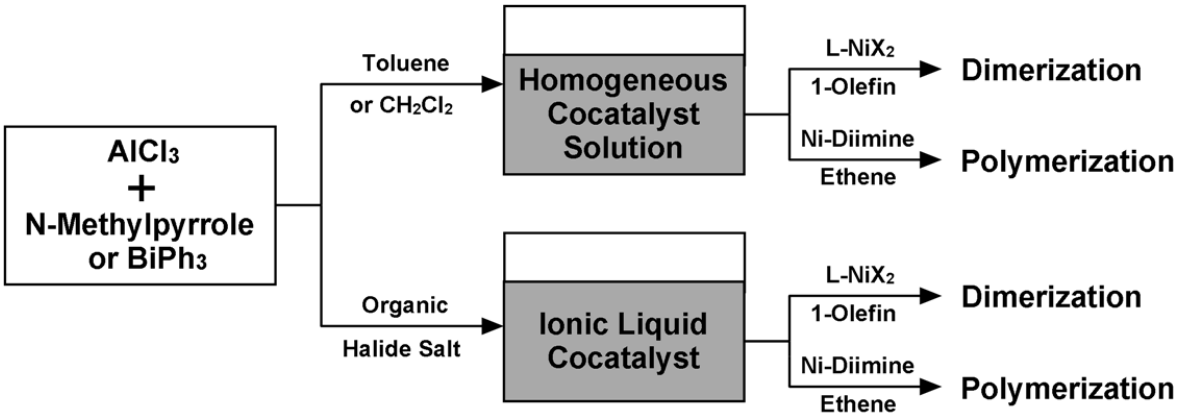
In order to minimize buffer leaching, we synthesized cationic *para*-trimethylammonium substituted triphenylphosphine derivatives employing either an oxide or a borane protecting group. The cationic triphenylphosphine buffer with an iodide anion showed an increased solubility in Lewis acidic chloroaluminate ionic liquids compared to the hardly soluble triphenylphosphine. The resulting buffered ionic liquids displayed improved dimer selectivities in biphasic propene dimerization reactions with nickel complexes. Further, the interaction of the cationic phosphine buffer with the ionic liquid was monitored by means of ^{31}P NMR spectroscopy. The line width of the ^{31}P NMR signal was found to be dependent on the degree of Lewis acidity of the chloroaluminate melt.

3.3 Nickel Catalyzed Propene Dimerization Reactions in $BiPh_3$ Buffered Chloroaluminate Ionic Liquids: High Performance with Unconventional Cations



In the course of our search for optimized compositions, chloroaluminate melts with variable Lewis acidities and $BiPh_3$ buffer contents were screened towards their performances in biphasic nickel catalyzed selective propene dimerization reactions. Slightly acidic, highly buffered systems yielded extremely selective propene dimerization systems. However, even low melting, highly Lewis acidic compositions were successfully buffered to give more than 90% dimers from propene. In combination with the melting point reduction of chloroaluminate melts upon addition of $BiPh_3$, it was possible to synthesize and screen 100 different organic halide salts for their performances in nickel catalyzed selective propene dimerization reactions with highly Lewis acidic compositions. Various nickel compounds were employed as catalyst precursors to yield similar catalytic performances. While lower reaction temperatures came along with higher dimer selectivities, the presence of sterically demanding tricyclohexylphosphine ligands led to the formation of valuable branched products.

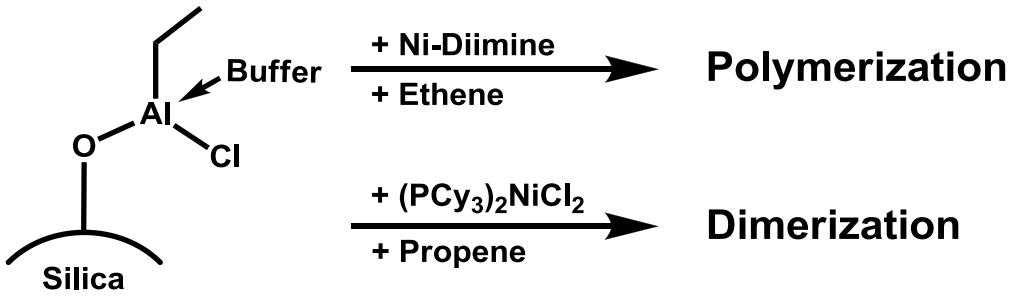
3.4 Buffered Aluminum Chloride as Highly Efficient Cocatalyst for Olefin Dimerization and Polymerization Reactions



After the promising results of the biphasic experiments, we tried to transfer the principle of donor-acceptor interactions between weak organic bases and $AlCl_3$ in ionic liquid cocatalysts to homogeneous systems. In combination with stoichiometric amounts of $BiPh_3$ or N-methylpyrrole buffer, aluminum chloride dissolved in toluene and methylene chloride to form a highly efficient and air stable cocatalyst for nickel complexes. Depending on the ligand structure of the nickel catalyst precursor, the resulting catalyst compositions were able to either polymerize ethene or to selectively dimerize various α-olefins. Further, the Lewis acidities of these binary homogeneous cocatalyst solutions

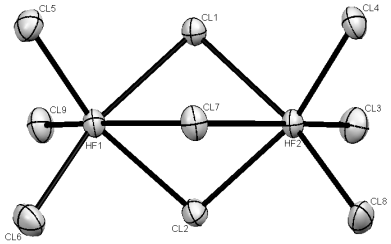
could be tuned precisely by the choice of the solvent and the type and amount of buffer. The properties of the produced polyethylenes could be influenced by the cocatalyst compositions. Also, the buffer sufficiently suppressed isomerization reactions of the α-olefinic products and hindered the ligand abstraction from the active nickel catalyst by $AlCl_3$ or the Lewis acidic ionic liquid. The donor-acceptor interaction between $BiPh_3$ or N-methylpyrrole and $AlCl_3$ was monitored by ^{27}Al NMR spectroscopy. Ethene polymerization also occurred in buffered chloroaluminate ionic liquids in the presence of a nickel diimine complex.

3.5 Silica Supported Cocatalysts for Olefin Dimerization and Polymerization Reactions with Nickel Complexes



In combination with $BiPh_3$ or N-methylpyrrole buffers, $EtAlCl_2$ or Et_2AlCl surface modified silicas were successfully employed as heterogeneous cocatalysts for nickel complexes to catalyze selective olefin dimerization reactions. The buffered heterogeneous cocatalysts were also able to activate a nickel diimine complex for ethene polymerization reactions. The active nickel species were immobilized at the silica surface to produce a granular polyethylene-silica composite material with a homogeneous particle size distribution. Further, surface modified silica was coated with a $BiPh_3$ buffered chloroaluminate ionic liquid to give a supported ionic liquid phase (SILP) cocatalysts for nickel catalyzed olefin dimerization reactions.

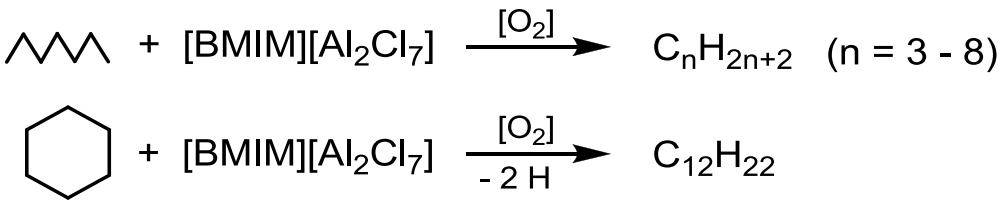
3.6 Solubility Behaviour of $TiCl_4$, $ZrCl_4$, and $HfCl_4$ in Chloroaluminate Ionic Liquids



$$2\ [Cation]^+[AlCl_4]^- \xrightarrow{+2\ HfCl_4} \begin{matrix}[Cation]^+[Hf_2Cl_9]^- \\ [Cation]^+[Al_2Cl_7]^-\end{matrix}$$

In the course of the ionic liquid cocatalyst development, we found that up to stoichiometric amounts of $ZrCl_4$ and $HfCl_4$ dissolved in a neutral chloroaluminate melt. The high Lewis acidities of the resulting solutions accrued from the formation of $[Al_2Cl_7]^-$ anions from $[AlCl_4]^-$ in the presence of $ZrCl_4$ or $HfCl_4$. From such ternary mixtures, crystals of $[Ti_2Cl_{10}][BMIM]_2$, $[Zr_2Cl_{10}][BMIM]_2$, and $[Hf_2Cl_9][PhNMe_3]$ were obtained, and their crystal structures were determined.

3.7 Oxidative Coupling and Catalytic Cracking of Alkanes in Lewis Acidic Chloroaluminate Ionic Liquids Enhanced by Molecular Oxygen



While experimenting with our highly Lewis acidic chloroaluminate ionic liquid cocatalysts for biphasic olefin dimerization reactions, we observed that saturated hydrocarbons like *n*-heptane were efficiently cracked in the presence of molecular oxygen. In dry air, the conversion of *n*-heptane to give mainly gaseous alkanes was more than one order of magnitude higher compared to systems with inert atmosphere. Further, cyclic alkanes were oxidatively coupled in the presence of O_2 under the consumption of two hydrogen atoms, while the same reactions only yielded skeletal isomers in argon atmosphere.

3.8 Individual Contribution to Joint Publications

The results presented in this thesis were obtained in collaboration with others and are to be submitted as indicated below. In the following, the contributions of all the co-authors to the different publications are specified. The asterisk denotes the corresponding author.

Chapter 4

This work is to be submitted with the title

“Heavy Metal with Heavy Impact: Olefin Dimerization Reactions in Triphenylbismuth Buffered Chloroaluminate Ionic Liquids”

Matthias Dötterl and Helmut G. Alt*

I synthesized all compounds, ionic liquids and performed the catalytic experiments presented in this work. I also wrote the publication. Christian Görl was involved in mechanistic discussions. Helmut G. Alt corrected and commented the manuscript.

Chapter 5

This work is to be submitted with the title

“Facile Synthesis of new Cationic Triphenylphosphine Derivatives and their Use for Propene Dimerization Reactions in Buffered Chloroaluminate Ionic Liquids”

Matthias Dötterl, Peter Thoma, and Helmut G. Alt*

I synthesized all compounds, ionic liquids and performed the catalytic experiments. Further, I wrote the publication. I also characterized all products. Peter Thoma helped me measuring the NMR spectra of heteroatoms and was involved in scientific discussions, comments and correction of the manuscript. Helmut G. Alt corrected and commented the manuscript.

Chapter 6

This work is to be submitted with the title

“Nickel Catalyzed Propene Dimerization Reactions in $BiPh_3$ Buffered Chloroaluminate Ionic Liquids: High Performance with Unconventional Cations”

Matthias Dötterl and Helmut G. Alt*

I synthesized all compounds, ionic liquids and performed the catalytic experiments. Further, I wrote the publication. Helmut G. Alt corrected and commented the manuscript.

Chapter 7

This work is to be submitted with the title

“Buffered Aluminum Chloride as Highly Efficient Cocatalyst for Olefin Dimerization and Polymerization Reactions”

Matthias Dötterl and Helmut G. Alt*

I synthesized all compounds, ionic liquids and performed the catalytic experiments. Further, I wrote the publication. Peter Thoma helped me measuring the ^{27}Al NMR spectra. Winfried Kretschmer did the high temperature GPC measurements. Helmut G. Alt corrected and commented the manuscript.

Chapter 8

This work is to be submitted with the title

“Silica Supported Cocatalysts for Olefin Dimerization and Polymerization Reactions with Nickel Complexes”

Matthias Dötterl and Helmut G. Alt*

I synthesized all compounds, ionic liquids and performed the catalytic experiments. Further, I wrote the publication. Winfried Kretschmer did the high temperature GPC measurement. Helmut G. Alt corrected and commented the manuscript.

Chapter 9

This work is to be submitted with the title

"Solubility Behaviour of $TiCl_4$, $ZrCl_4$, and $HfCl_4$ in Chloroaluminate Ionic Liquids"

Matthias Dötterl, Isabelle Haas, and Helmut G. Alt*

I synthesized all compounds, ionic liquids and performed the catalytic experiments. Further, I wrote the publication. Germund Glatz, Tobias Bauer and Isabelle Haas performed one X-ray analysis each and solved the crystal structures. Isabelle Haas helped me utilizing the X-ray data. Helmut G. Alt corrected and commented the manuscript.

Chapter 10

This work is to be submitted with the title

"Oxidative Coupling and Catalytic Cracking of Alkanes in Lewis Acidic Chloroaluminate Ionic Liquids Enhanced by Molecular Oxygen"

Matthias Dötterl and Helmut G. Alt*

I synthesized all compounds, ionic liquids and performed the catalytic experiments. Further, I wrote the publication. Helmut G. Alt corrected and commented the manuscript.

4 Heavy Metal with Heavy Impact: Olefin Dimerization Reactions in Triphenylbismuth Buffered Chloroaluminate Ionic Liquids

Matthias Dötterl[a] and Helmut G. Alt*[a]

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Keywords: ionic liquids, chloroaluminates, nickel, biphasic catalysis, dimerization

Manuscript to be submitted (Communication)

4.1 Main Text

Since ionic liquids received broader attention as a new class of reaction media in the 1980s,[1] when $AlCl_3$ based systems were thoroughly investigated, many generations of air and water stable ionic liquid systems have been developed.[2] At present, there are numerous ionic liquid based systems and processes that have found applications in industry.[2b, 3] However, many of the newly developed systems with improved stabilities and properties are based on ionic liquids containing uncommon anions. These ionic liquids are very expensive, especially when fluorine atoms are involved. Thus, it is not a big surprise that the largest industrial processes still rely on cheap first generation chloroaluminate systems.

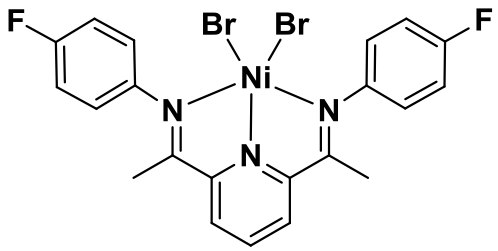
PetroChina's Ionikylation® process uses a composite $AlCl_3$ / CuCl ionic liquid, which catalyzes the alkylation of isobutane with butenes. The process is currently operated in an 65000 t/a alkylation unit in China.[4]

Chauvin *et al.* developed a process for biphasic catalytic dimerization reactions of short chain olefins in the 1990s.[5] The ionic liquid made from N,N'-alkylmethylimidazolium chloride mixed with aluminum chloride and ethylaluminum dichloride plays a dual role as cocatalyst and solvent for the catalytically active nickel complex. The Institut Français du Pétrole (IFP) brought this so called DIFASOL® process to industrial application by retrofitting it to their existing DIMERSOL® units.[6] In the year 2009, 35 DIMERSOL® units have been licensed[7] for selective dimerization reactions of C_3 and C_4 olefinic cuts.[6c] Typically, these processes are operated with capacities between 20000 and 90000 t/a. The biphasic DIFASOL® process provides several advantages over its homogeneous DIMERSOL® analogue, which is based on nickel complexes activated with $EtAlCl_2$ in solution.[8] The nickel catalyst and most of the alkylaluminum species remain within the ionic liquid phase. Thus, the nickel and aluminum consumption is greatly reduced. DIFASOL® shows higher selectivities to give dimers and can be operated with streams containing smaller amounts of olefins. In combination with a much smaller reactor size, this leads to greatly improved process economics.[6b, 6c]

Besides DIFASOL®, which uses ethylaluminum groups to suppress uncontrolled cationic olefin oligomerization reactions in solely $AlCl_3$ based ionic liquids,[9] Wasserscheid *et al.* developed a system buffered by weak organic bases.[10] Pyridine, quinoline and pyrrole derivatives were added to slightly acidic chloroaluminate ionic liquids. The interaction of the Lewis bases with $AlCl_3$ or the $[Al_2Cl_7]^-$ species present in such liquids[1a, 11] reduced the "latent acidity".[12] The interaction prevented uncontrolled cationic olefin oligomerization reactions. A chloroaluminate liquid buffered with weak organic bases was successfully employed to activate nickel complexes for dimerization reactions of 1-butene. In a recent article, Wasserscheid *et al.* extended the system to propene and 1-hexene dimerization reactions and studied the kinetics of these biphasic reactions in detail.[13] They found that the reaction rates are strongly limited by mass transfer of the substrate olefins.

Following the concept of Lewis base buffered systems we found that triarylamine, triarylphosphine and triarylbismuth compounds efficiently buffer ionic liquids derived

from $AlCl_3$. The dissolution of small amounts of these buffering substances in a slightly acidic 1-butyl-3-methylimidazolium (BMIM) chloroaluminate ionic liquids ($AlCl_3$ / BMIMCl = 1.20) yielded the ionic liquid cocatalysts. The air stable bis(imino)pyridine complex of nickel(II)bromide (**Figure 1**) was used as nickel source. It readily dissolved in the buffered ionic liquids and the resulting ionic liquid catalysts dimerized propene in batch experiments with high productivities and selectivities (**Table 1**).



1

Figure 1: Catalyst precursor used for biphasic propene dimerization reactions.

We substituted the term “activity” with “productivity” following the results of Wasserscheid *et al.*[13] They showed that above a certain concentration, the activities of the systems did not depend on the amount of catalyst anymore due to mass transport limitations. The activities were then even independent from the temperature. For our system we chose a catalyst concentration of 10^{-5} $mol_{catalyst}$ / $g_{ionic\ liquid}$. A data set of a catalyst concentration series can be found in the Supporting Information. The minimum catalyst concentration that still influenced the overall activity in the investigated systems was found to be around 10^{-6} $mol_{catalyst}$ / $g_{ionic\ liquid}$. Thus, the productivities could be calculated as the amount of products formed by one gram of active liquid in one hour under the assumption that the productivities of the systems did not depend on the catalyst concentration. For a typical catalytic experiment, 2 – 4 ml ionic liquid were mixed with the corresponding amount of buffer followed by the addition of the catalyst precursor (**1**). Between 2.5 and 4 g of the resulting homogeneous solutions were used for the experiments.

Table 1: Nickel catalyzed biphasic propene dimerization reactions in buffered acidic 1-butyl-3-methylimidazolium (BMIM) chloroaluminate ionic liquids.[1]

No.	Buffer	[Buffer] / [BMIMCl]	Productivity[2]	Dimers [%]
1	NPh_3	0.12	4.0	81.0
2	PPh_3	0.12	> 15.0[3]	93.6
3	$AsPh_3$	0.12	0	–
4	$SbPh_3$	0.12	6.8	Oil[4]
5	$BiPh_3$	0.07	> 10.8[3]	89.2
6	$BiPh_3$	0.12	> 10.8[3]	93.1
7	$BiPh_3$	0.30	6.7	96.0

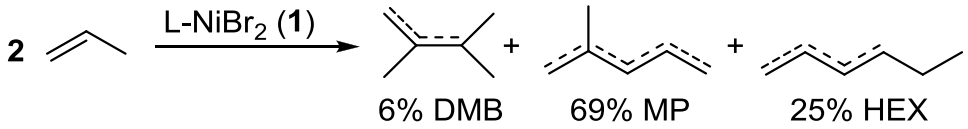
[1] Reaction conditions: 2 ml of ionic liquid with [$AlCl_3$] / [BMIMCl] = 1.20; catalyst precursor 1; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Complete conversion. [4] Higher oligomers derived from a cationic oligomerization reaction.

While the triphenylamine buffered system produced only 81% dimers (1), the triphenylphosphine based system with the same composition gave 94% dimers (2). However, the solubility of PPh_3 strongly depended on the temperature. At 25°C, PPh_3 did not dissolve completely in the ionic liquid. Due to its nonpolar character, triphenylphosphine systems suffered from heavy leaching into the organic product phase. Thus, the results strongly depended on the amount of olefin or the reaction temperature and, therefore, displayed a bad reproducibility. The addition of $AsPh_3$ deactivated the system (3), while $SbPh_3$ (4) showed no ability to prevent cationic olefin oligomerization reactions induced by the highly Lewis acidic aluminum centers.[9]

Unexpectedly, the triphenyl compound of the last element in the row, bismuth, proved to be a perfect buffer. Starting from a concentration of 0.07 equivalents of $BiPh_3$, the $BiPh_3$ buffered systems produced dimers with high selectivities (5 – 7). It was completely soluble in chloroaluminate ionic liquids, even at higher ratios. There are three reasons for its high solubility. First, aromatic compounds readily dissolve in chloroaluminate ionic

liquids driven by an interaction of the π-electrons with the Lewis acidic $[Al_2Cl_7]^-$ centers.[14] Second, the free electron pair interacts with the aluminum centers keeping the buffer within the ionic liquid phase. The last and probably most important reason is the polarity of $BiPh_3$. In contrast to PPh_3, it hardly dissolves in saturated hydrocarbon phases, and even its solubility in olefins like 1-hexene is strongly limited. Once mixed in the ionic liquid phase, the system remained stable over extended periods of time.

All experiments performed with catalyst precursor **1** yielded a similar dimer distribution (**Scheme 1**), which accompanies with the results of Wasserscheid *et al.*[13] Most probably, the ligand was abstracted and a typical product distribution assigned to a ligand free nickel salt was obtained.



Scheme 1: Product distribution of the hexene fraction obtained with all biphasic propene dimerization reactions (± 2%) in $BiPh_3$ buffered chloroaluminate ionic liquids catalyzed by complex **1** (DMB = 2,3-dimethylbutenes; MP = 2-methylpentenes; HEX = *n*-hexenes; possible double bond positions indicated by dots).

Since $BiPh_3$ is also a non volatile and air stable solid, it is predestined to adjust the acidities of chloroaluminate ionic liquid systems precisely. While only slightly acidic chloroaluminate melts were chosen for nickel catalyzed dimerization reactions by other groups, we extended our $BiPh_3$ buffered systems to maximum acidic compositions ($AlCl_3$ / chloride salt = 2, **Table 2**). Surprisingly, 0.12 equivalents of $BiPh_3$ buffer successfully suppressed cationic olefin oligomerization reactions in such highly acidic melts, too (9). With higher buffer contents, selectivities around 90% were obtained (10, 11).

The use of highly acidic melts is advantageous since usually, the melting points of chloroaluminate melts display a minimum at that composition.[15] Close to equimolar chloride salt / $AlCl_3$ ratios, the melting points increase drastically. Therefore, mostly cations yielding low melting systems were chosen, e.g. imidazolium or pyridinium salts. When $BiPh_3$ was added to chloroaluminate melts, the melting points were further

decreased. The additive acted like an additional solvent diluting the ionic liquid. In combination with the use of maximum acidic compositions, it was possible to create catalytically active systems from unconventional and cheap cations, which would mostly form “ionic solids” at ambient temperature (**Table 3**, experiment 18).

Table 2: Nickel catalyzed biphasic propene dimerization reactions in $BiPh_3$ buffered acidic 1-butyl-3-methylimidazolium (BMIM) chloroaluminate ionic liquids.[1]

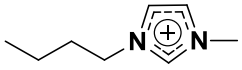
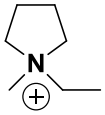
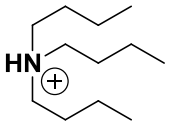
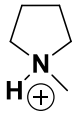
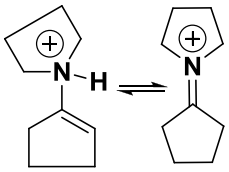
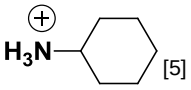
No.	Composition [BMIMCl] / [$AlCl_3$] / [$BiPh_3$]	Productivity[2]	Dimers [%]
8	1.00 / 1.20 / 0.12	> 10.8[3]	93.1
9	1.00 / 2.00 / 0.12	> 11.4[3]	74.8
10	1.00 / 2.00 / 0.30	> 9.3[3]	85.5
11	1.00 / 2.00 / 0.60	> 11.5[3]	90.6

[1] Reaction conditions: 2.5 – 3.5 g buffered ionic liquid; catalyst precursor 1; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Complete conversion.

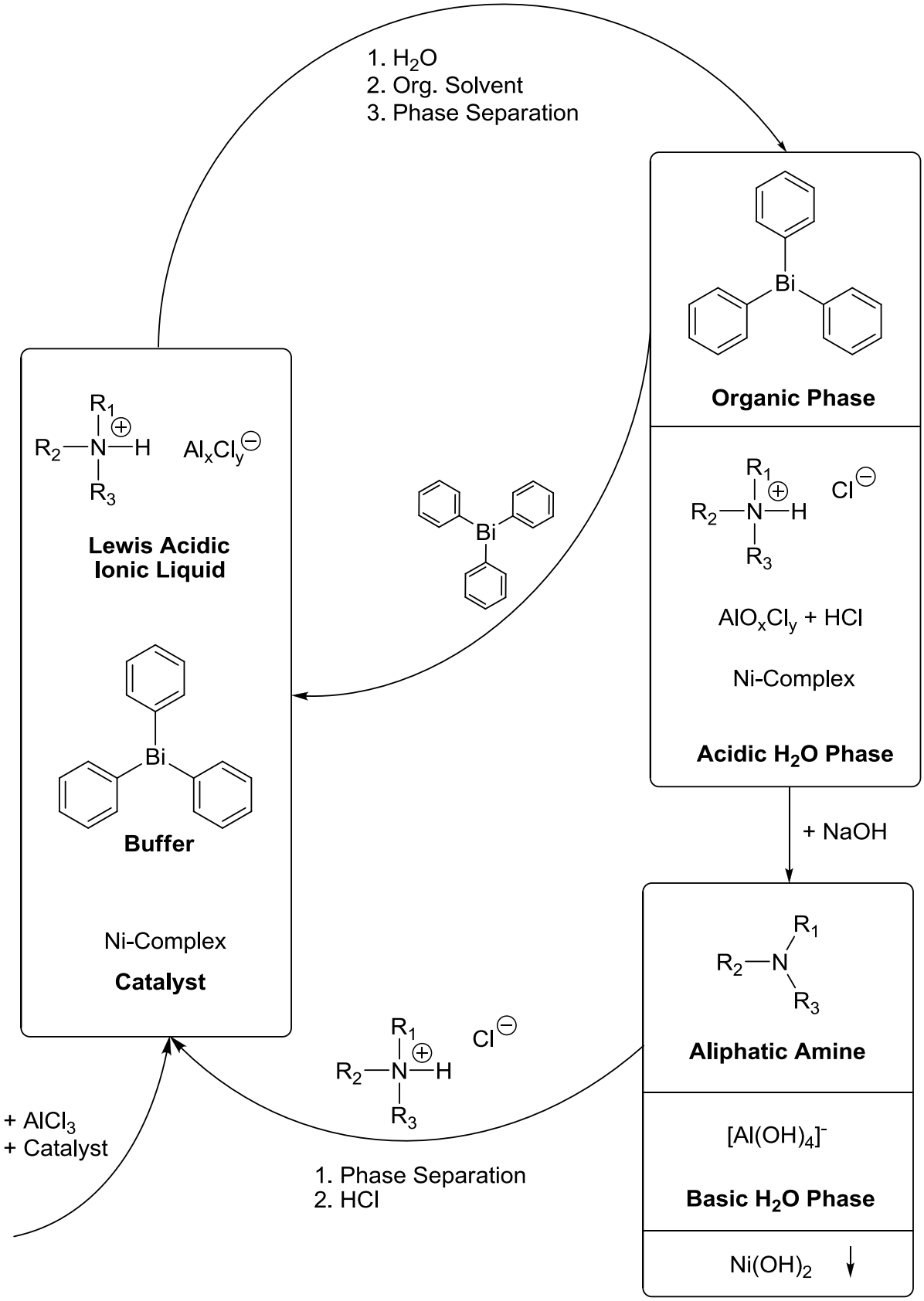
The screening of several cations is summarized in **Table 3**. The choice of the cation was crucial for the catalytic performances. It influenced the solubility of the buffer and the substrate. Because no alkylaluminum groups were present in the systems, even amine hydrochlorides could be used (15 – 18). This is a huge advantage over the commercial DIFASOL® system since, in principle, it makes the systems stable in air. N-methylpyrrolidine hydrochloride (16) gave the best performance in terms of selectivity and lifetime among the chloride salts tested. After each experiment the product phase was decanted. The system displayed a constant selectivity of more than 90% over seven runs without further addition of $BiPh_3$.

In general, higher productivities came along with lower selectivities, while more selective systems were less productive. However, the desired selectivities could be adjusted simply by varying the buffer content.

Table 3: Cation screening for nickel catalyzed biphasic propene dimerization reactions in $BiPh_3$ buffered acidic chloroaluminate ionic liquids.[1]

No.	Cation	Productivity[2]	Dimers [%]
12		> 9.9[3]	90.0
13		> 10.2[3]	86.2
14		7.8	92.0
15		> 10.6[3]	89.4
16		7.6[4]	91.6
	Run 2	8.2	93.5
	Run 3	7.5	93.3
	Run 4	7.6	93.1
	Run 5	8.1	93.1
	Run 6	8.7	91.8
	Run 7	> 11.2[3]	91.1
17		> 10.9[3]	90.0
18	 [5]	> 8.8[3]	76.1

[1] Reaction conditions: 3.0 – 4.0 g buffered ionic liquid; composition $[BiPh_3]$ / $[cation]^+[Al_2Cl_7]^-$ = 0.30; catalyst precursor 1; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Complete conversion. [4] Products decanted after each run. [5] Ionic liquid without buffer solid at ambient temperature.



Scheme 2: Suggested recycling of depleted buffered chloroaluminate ionic liquids: recovery of $BiPh_3$ and a water insoluble amine by acid base extraction.

The possibility to use simple hydrochlorides facilitates the recycling of depleted catalytic systems. Amines as well as the water insoluble $BiPh_3$ can be recovered by a simple acid base extraction as depicted in **Scheme 2**. The hydrolysis of depleted systems yields an acidic aqueous phase, from which the water insoluble $BiPh_3$ can be extracted with an organic solvent. A simple pH change afforded by the addition of e.g. sodium hydroxide releases the free amine. In the case of very nonpolar amines like Bu_3N, whose solubility in water at 20°C is less than 0.1%,[16] the amines can be recovered by a simple phase separation. For water miscible amines, distillation yields the amine, which then can be converted to its hydrochloride again.

After the optimization of our system, we tested a maximum Lewis acidic N-methyl-pyrrolidine hydrochloride based ionic liquid for the dimerization reactions of α-olefins from ethene to 1-hexene in a 300 ml Parr stainless steel autoclave. Buffer contents of 0.15 and 0.30 equivalents relative to the amount of the cation were employed for each olefin (**Table 4**). As expected, higher chain lengths of the olefins reduced the productivities due to the lower solubility of the substrate.[13] For the most productive systems, it was possible to keep the reaction temperature at 40°C by intensive cooling due to the combination of extremely high reaction rates and strongly exothermic reactions. Both reactions were stopped early. In the case of ethene, the reactor reached its capacity after 40 minutes (19). For propene, the conversion reached 100% after about 30 minutes (21), indicated by a drop to ambient pressure.

The system is ideal for dimerization reactions of olefins up to 1-butene and keeps up with the performance of the commercial DIFASOL® system. All olefins were dimerized with high selectivities. Triphenylbismuth buffered chloroaluminate systems provide superior alternatives to other ionic liquid based systems used for olefin dimerization reactions. The catalytic performance can be adjusted by varying the buffer content, depending if high productivities or high dimer selectivities are required. Dimer selectivities of 90% and more can be achieved easily, still with high productivities.

Table 4: Nickel catalyzed biphasic dimerization reactions of several olefins in $BiPh_3$ buffered [N-methylpyrrolidinium]$^+$[Al_2Cl_7]$^-$ melts.[1]

No.	Olefin	[$BiPh_3$] / [Cation]	Dimers [%]	Productivity[2]
19	Ethene	0.15	62.7[3]	62.6[4]
20	Ethene	0.30	81.7[5]	6.8
21	Propene	0.15	83.7	> 110.7[6]
22	Propene	0.30	93.7	18.5
23	1-Butene	0.15	77.9	19.2
24	1-Butene	0.30	89.3	8.3
25	1-Hexene	0.15	95.0	2.4
26	1-Hexene	0.30	98.3	0.4

[1] Reaction conditions: 2.5 – 4.0 g buffered ionic liquid; catalyst precursor 1; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 40°C; stirring rate = 600 min^{-1}; t = 60 min; stirred 300 ml Parr stainless steel autoclave; 200 ml liquid olefin; 10 bar ethene and 35 g *n*-heptane solvent for ethene experiments. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] 28.0% 1-butene. [4] Calculated for 60 min; reactor capacity reached after 40 min. [5] 46.8% 1-butene. [6] Calculated for 60 min; complete conversion after about 30 min.

Also, the systems are insensitive towards oxygen. Ionic liquids exclusively consisting of $AlCl_3$ are not sensitive to air, unlike alkylaluminum containing systems. The latter even contribute to the deactivation of Ni(II) catalysts by reducing Ni(II) to its zero oxidation state.[17] Triphenylbismuth is also stable and can be handled in air. Due to the absence of alkylaluminum groups, a wide range of amine hydrochlorides can be used. The scope of ammonium salts is further extended because $BiPh_3$ decreases the melting points of chloroaluminate ionic liquids.

The biggest advantage, however, is the easy recycling of depleted dimerization systems. Just very cheap $AlCl_3$ is consumed (**Scheme 2**). Both amine and buffer can be recovered. Due to the facile recycling, it is not necessary to remove all impurities from an olefin stream meticulously. The accumulation of impurities in the ionic liquid catalyst

phase is a major problem of DIFASOL® systems. Therefore, they are operated in combination with DIMERSOL® reactors, which totally purify the DIFASOL® feed.[6c]

However, the absence of any alkylaluminum compounds arose questions about the dimerization mechanism. In the literature, a mechanism is generally accepted for two-valent nickel complexes that involves Ni–H or Ni–C bonds.[7, 18] In all of these cases it was assumed that the nickel center is alkylated by the aluminum cocatalyst to form nickel hydride or nickel alkyl species. Alternatively, Ni–C bond containing species like η^3-allyl nickel compounds were employed.[18g] The olefins coordinate to a free coordination site at the square planar nickel center and are inserted into the Ni–H or Ni–C bond. Yet, this mechanism could not be applied to our system. Besides a nickel salt, buffered chloroaluminate melts only contained $AlCl_3$, an organic halide salt and the buffer. None of these is able to form either Ni–H or Ni–C bonds from nickel halide salts. Also, the reduction of Ni(II) to give Ni(I) or Ni(0) species was unlikely in these systems. For nickel compounds in lower oxidation states than two, alternative mechanisms were also discussed. For example, nickel(I) compounds are involved in selective olefin oligomerization reactions with nickel impregnated metal oxides. For this reaction, a nickelacyclopentane was proposed, which is in equilibrium with the corresponding di-olefin complex. The rate determining step was assumed to be the decomposition of the metallacycle to yield the dimer upon reductive elimination.[19] For Ni(0), metallacycles are also well known.[20]

Since the product distribution resulting from selective propene dimerization reactions with catalyst precursor **1** matched the results for ligand free nickel salts,[13] we expected that the ligand was abstracted. Nickel halides were found to form $Ni(AlCl_4)_2$[21] or $[Ni(AlCl_4)_3]^-$,[22] if they were mixed with aluminum chloride or acidic chloroaluminate ionic liquids, respectively. In buffered chloroaluminate melts used for olefin dimerization reactions, these weakly coordinating tetrachloroaluminate anions are expected to be easily replaced by other ligands like buffer or olefin molecules (**Figure 2**).

Considering our catalytic results, we propose a new mechanism for nickel catalyzed olefin dimerization reactions in buffered, alkylaluminum free chloroaluminate ionic liquids using the example of ethene (**Scheme 3**). Similar to the mechanism proposed for Ni(I),[19] we expect the formation of a metallacycle, which is in equilibrium with a $Ni(ethene)_2$ complex. Decomposition of the metallacycle through β-H elimination yields

an ω-alkenyl stabilized nickel hydride species. Elimination followed by the coordination of a new ethene molecule results in a nickel di-olefin complex with ethene and 1-butene being coordinated to the nickel center. At this point, there are two possible pathways. For weakly buffered, more acidic compositions, 1-butene remains at the nickel center and forms an ethyl branched nickelacyclopentane again. This route would lead to the formation of branched, higher oligomers from ethene. Yet, if the system is highly buffered, we expect the buffer to compete with 1-butene for the coordination site at the active nickel center. Since the coordination strength of 1-butene is weaker compared to ethene, 1-butene is replaced by a buffer molecule. The also weakly coordinating buffer molecule can be substituted again by an ethene molecule to form the initial $Ni(ethene)_2$ species.

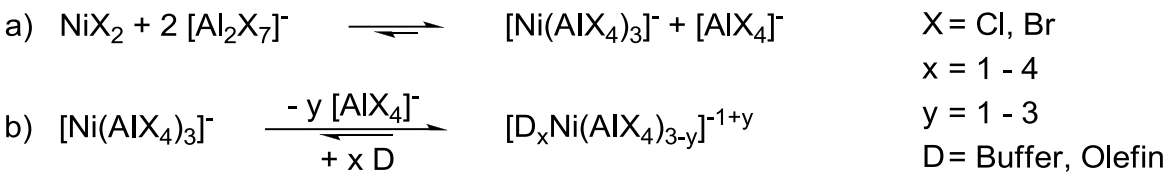
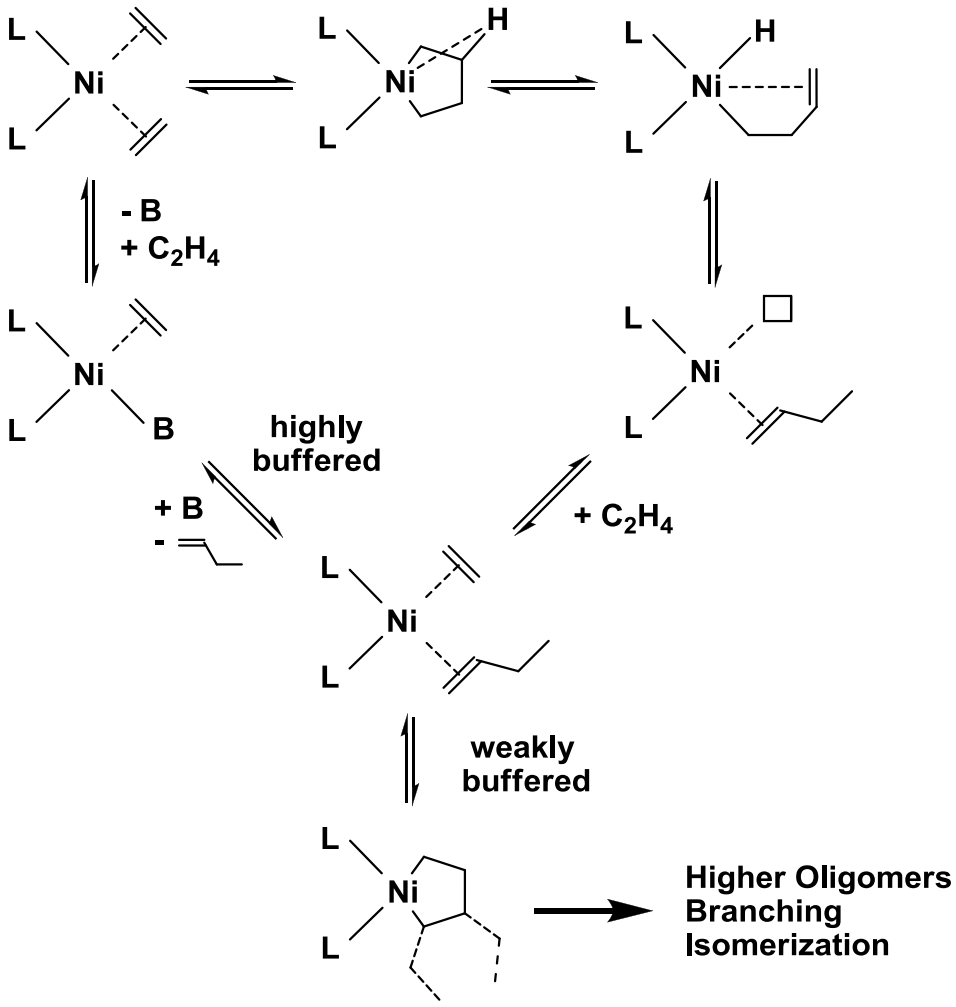


Figure 2: Formation of $[Ni(AlX_4)_3]^-$ from nickel halide salts in acidic haloaluminate ionic liquids (a) and exchange of the weakly coordinating tetrahaloaluminate ligands by competing donor molecules (b).

Although we have no experimental evidence for the oxidation state of the active nickel catalyst, we propose that the active species is Ni(II). Due to the formation of weakly coordinating tetrahaloaluminate anions in acidic ionic liquids,[22] the Ni(II) center is easily accessible. The mechanism conveniently includes a metallacycle as well as a Ni–H species. Also, our results indicated that the original product from ethene dimerization reactions was 1-butene. However, subsequent isomerization reactions disguised the real product distributions. This became clear since the selectivity to give 1-butene increased from 28% (19) to 47% (20) with twice the amount of buffer. Thus, the buffer did not only buffer Lewis acidic aluminum species, it also favoured the formation of dimers and suppressed subsequent isomerization reactions.



Scheme 3: Proposed mechanism for nickel catalyzed ethene dimerization reactions in buffered chloroaluminate ionic liquids (L = any ligand, B = buffer molecule).

Finally, an $EtAlCl_2$ based chloroaluminate ionic liquid similar to a commercial DIFASOL® composition[23] was modified with our $BiPh_3$ buffer and tested in batch propene dimerization reactions (**Table 5**). The unmodified system gave about 80% dimers (27) with catalyst precursor **1**. If small amounts of $BiPh_3$ were dissolved in that system, the dimer yield jumped to almost 97%. The addition of 0.03 equivalents (30) gave the best result in combination with a high productivity. If too much buffer was added, the productivities were reduced (28, 29), while no effect could be observed with only 0.01 equivalents (31) of $BiPh_3$.

Table 5: Nickel catalyzed biphasic propene dimerization reactions in typical DIFASOL® systems modified with $BiPh_3$. [1]

No.	[$EtAlCl_2$] / [BMIMCl]	[$BiPh_3$] / [BMIMCl]	Productivity[2]	Dimers [%]
27	0.20	0	> 18.1[3]	79.6
28	0.20	0.12	2.0	96.8
29	0.20	0.06	7.1	94.6
30	0.20	0.03	> 19.4[3]	94.1
31	0.20	0.01	> 13.0[3]	79.4
32	0	0.12	> 10.8[3,4]	93.1

[1] Reaction conditions: 2.5 – 4.0 g buffered ionic liquid; [$AlCl_3$] / [BMIMCl] = 1.20; catalyst precursor 1; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 45 min; 300 ml glass autoclave; 40 – 60 ml liquid propene. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Complete conversion. [4] Reaction time 60 minutes.

The combination of $EtAlCl_2$ and $BiPh_3$ with $AlCl_3$ based ionic liquids provides a promising, highly active and selective nickel catalyzed dimerization system for commercial applications. The fact that $BiPh_3$ reduces the melting temperatures of said systems opens the door for the application of a wide range of cheap cations.

The possibility to tune the Lewis acidities and to suppress subsequent isomerization reactions simply by varying the $BiPh_3$ content should make $BiPh_3$ buffered chloroaluminate ionic liquids interesting for many other types of reactions like Friedel Crafts alkylations, acylations, isomerizations, hydrogenations,[2b, 24] and many more.

Supporting Information Available

Detailed experimental procedures, the preparation of the ammonium salts, ionic liquids and complex **1** as well as a catalyst concentration series are described in the Supporting Information.

Acknowledgements

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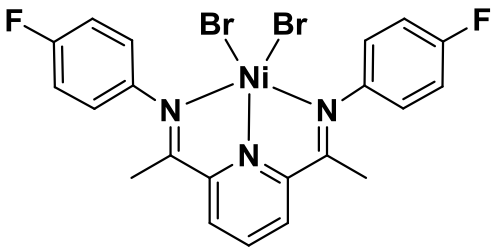
4.3 Supporting Information

General Remarks

All chemical manipulations were carried out using standard Schlenk techniques under argon atmosphere. *n*-Heptane was distilled from Na/K alloy under an atmosphere of argon. The products of the dimerization experiments were characterized by gas chromatography (Agilent 6850) and GC-MS (FOCUS DSQ™ Thermo Scientific). Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70 eV). Elemental analyses were performed with a VarioEl III CHN instrument. Acetanilide was used as a standard. Ethene (99.9%), propene (99.3%), and 1-butene (99.3%) were purchased from Riessner Gase, Lichtenfels, and were dried over a column packed with P_4O_{10}. 1-Hexene and $EtAlCl_2$ (0.9 M in heptane) were purchased from Acros and used without further purification. Triphenylamine, triphenylphosphine, triphenylarsine, triphenylantimony, triphenylbismuth, and cyclohexylamine hydrochloride were purchased from ABCR, 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium chloride, 1-pyrrolidino-1-cyclopentene, tributylamine, N-methylpyrrolidine, and $AlCl_3$ (ReagentPlus®) were purchased from Sigma-Aldrich and used as received. Chloroethane (Chloraethyl, Dr. Henning) was purchased in a local pharmacy.

Synthesis of Complex 1



1

The ligand precursor was synthesized from 2,6-diacetylpyridine and 4-fluoroaniline according to a literature procedure.[1] The ligand precursor (1.19 g) was dissolved in THF (100 ml) and 1.05 g of (dme)$NiBr_2$ were added. The mixture was stirred for 2 h at

ambient temperature. After most of the solvent had been removed in vacuo, the complex was precipitated by the addition of *n*-pentane (100 ml). After filtration and washing with *n*-pentane, complex **1** was obtained in quantitative yield as an orange brown solid.

EI-MS data: 567 ($M^{\bullet+}$) (1), 488 M –Br (33), 407 M –2Br (22), 349 M –$NiBr_2$ (65), 136 F-C_6H_4-N=C-CH_3 (100).

Elemental analysis (calculated, found for $C_{21}H_{17}Br_2F_2N_3Ni$): C (44.42, 44.51), H (3.02, 3.56), N (7.40, 7.05).

Synthesis of the Ionic Liquids

The ionic liquids were synthesized by directly mixing the corresponding amount of $AlCl_3$ and chloride salt in a cooled Schlenk tube. In the case of $EtAlCl_2$ containing systems, a 0.9 molar solution of $EtAlCl_2$ in heptane was added to the liquid and the solvent was removed in vacuo. The obtained ionic liquids were stored in Schlenk tubes.

Procedure for Dimerization Reactions Using Buffered Ionic Liquids

Prior to the experiments, 2 to 4 ml of the ionic liquid were filled into a Schlenk tube and mixed with the buffer. After the buffer had dissolved upon stirring, the nickel complex **1** was added. The obtained homogeneous solution was syringed into the reaction vessel. Its amount was determined by the weight difference of the syringe.

For the screening experiments with propene, a 300 ml glass autoclave equipped with a stirring bar and a magnetic stirrer with a stirring rate of 1200 min^{-1} was used. The glass autoclave was kept in a drying oven at 150°C for several hours before an experiment. After the addition of the active ionic liquid, propene (40 to 60 ml) was condensed into the glass autoclave by liquid nitrogen cooling. Then, the autoclave was placed in a metal box for safety reasons, and the temperature was regulated by an external water bath. After the experiment, the pressure was slowly released by opening a valve. The product fraction was filtered through a short plug of silica and analyzed by gas chromatography.

For the screening experiments in **Table 4** and **Table 6**, a stirred 300 ml Parr stainless steel autoclave was used. The steel vessel was kept in a drying oven at 150°C for

several hours before an experiment, and it was filled with argon. Then, the active ionic liquid was added under argon counter flow.

Ethene: *n*-Heptane was added to the reactor vessel under argon counter flow. The system was put under vacuum, and the temperature was raised to 40°C. Then, an ethene pressure of 10 bar was applied. Cooling of the highly exothermic reaction was achieved manually by an external liquid nitrogen cooled acetone bath. After the experiment, the vessel was quickly cooled to –20°C. The pressure was released, the weight difference of the vessel was determined, and a cooled sample was directly analyzed by gas chromatography.

Propene: The vessel was evacuated, and liquid propene (200 ml) was soaked into it at 77 K. The reaction was started by quickly heating the vessel to 40°C with boiling water. Cooling of the highly exothermic reaction was achieved manually by an external liquid nitrogen cooled acetone bath. After the experiment, the vessel was cooled to 0°C, and the pressure was slowly released. After reaching ambient temperature, the weight difference of the vessel was determined, and the product phase was analyzed by gas chromatography.

1-Butene: The vessel was evacuated, and liquid 1-butene (200 ml) was soaked into it at –20°C. The reaction was started by quickly heating the vessel to 40°C with boiling water. Cooling of the exothermic reaction was achieved manually by an external ice bath. After the experiment, the vessel was cooled to –20°C, and the organic phase was analyzed by gas chromatography. Productivities were calculated from the GC spectra.

1-Hexene was added to the reactor vessel, and the reactor was stirred at 40°C. After the experiment, the organic phase was analyzed by gas chromatography. Productivities were calculated from the GC spectra.

Synthesis of the Hydrochlorides of Tributylamine, 1-Pyrrolidino-1-cyclopentene and N-Methylpyrrolidine

The corresponding amines were dissolved in dry diethylether, and HCl gas was bubbled through the flask until no more gas was absorbed. The white, precipitated ammonium salts were filtered, washed three times with diethylether and *n*-pentane, dried in vacuo and used without further purification.

Synthesis of N-Ethyl-N-methylpyrrolidinium Chloride

N-ethyl-N-methylpyrrolidinium chloride was synthesized from chloroethane and N-methylpyrrolidine in acetonitrile following the procedure described for triethylamine in the literature.[2]

Catalyst Concentration Series

Table 6: Catalyst concentration series of nickel catalyzed biphasic propene dimerization reactions in $BiPh_3$ buffered acidic chloroaluminate ionic liquids.[1]

No.	Catalyst Concentration[2]	Productivity[3]	"Activity"[4]	Dimers [%]
32	10^{-5}	18.5	1.9	93.7
33	10^{-6}	18.2	18.2	92.9
34	10^{-7}	9.7	97.1	92.1
35	10^{-8}	1.9	192.1	92.2

[1] Reaction conditions: 3.5 – 4.5 g buffered ionic liquid; $[BiPh_3]$ / $[\text{N-methylpyrrolidinium}]^+[Al_2Cl_7]^-$ = 0.30; catalyst precursor 1; T = 40°C; stirring rate = 600 min^{-1}; t = 60 min; stirred 300 ml Parr stainless steel autoclave; 200 ml liquid propene. [2] $mol_{catalyst}$ / $g_{ionic\ liquid}$. [3] $g_{product}$ / $g_{ionic\ liquid}$ x h. [4] $t_{product}$ / $mol_{catalyst}$ x h.

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5 Facile Synthesis of new Cationic Triphenylphosphine Derivatives and their Use for Propene Dimerization Reactions in Buffered Chloroaluminate Ionic Liquids

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Keywords: ionic liquids, NMR spectroscopy, donor-acceptor systems, biphasic catalysis, dimerization

Manuscript to be submitted

Abstract: We describe the facile synthesis of new, cationic triphenylphosphine derivatives containing *para*-trimethylammonium substituents. The ionic phosphines were successfully employed in nickel catalyzed propene dimerization reactions in highly Lewis acidic chloroaluminate ionic liquids. Buffering of such liquids is achieved by an interaction of the Lewis basic phosphine with the Lewis acidic aluminum centers. The P–Al interaction of triarylphosphines and tri-*tert*-butylphosphine with the highly acidic ionic liquid [1-butyl-3-methylimidazolium]$^+$[Al_2Cl_7]$^-$ was monitored by ^{31}P and ^{27}Al NMR spectroscopy. Coupling of tri-*tert*-butylphosphine with ^{27}Al resulted in an expected but unusual sextet in the ^{31}P NMR spectrum and a doublet in the ^{27}Al NMR spectrum.

5.1 Introduction

Since green chemistry and sustainable processes have become an important aspect for industrial applications, phosphines with polar or ionic substituents attracted more and more attention. The first large scale application of phosphine ligands with ionic substituents is the Ruhrchemie/Rhône-Poulenc process used for hydroformylations reactions of short chain olefins. The rhodium catalyst is complexed by water soluble tris(*m*-sulfonylphenyl)phosphine (TPPTS) ligands and immobilized in an aqueous phase.[1] The product phase consisting of aldehydes is insoluble in the catalyst containing aqueous phase and can be separated by decantation. Simple product separation in combination with facile recycling of the catalyst reduces the process costs about 10% compared to the homogeneous process based on organic solvents.[2] Besides the sulfonated triphenylphosphine ligands, several other phosphines with different functional groups were employed in rhodium catalyzed hydroformylation reactions of olefins.[3] The application of ionic phosphines was also reported for several palladium catalyzed cross coupling reactions.[4] The field of ionic phosphines and their application in metal catalyzed reactions in water has been reviewed twice.[5]

Besides the reactions in water, the field of ionic liquids has emerged as new medium for catalyst immobilization and biphasic reactions.[6] Wasserscheid *et al.* developed the supported ionic liquid phase (SILP) concept for hydroformylation reactions. The active rhodium species are immobilized in an ionic liquid by polar phosphine ligands. A thin film of catalyst containing ionic liquid coated on an inorganic support acts as homogeneous biphasic catalytic system with the advantages of a heterogeneous system. The obtained powder can be used in fixed bed systems, and the product and catalyst separation becomes unnecessary.[7]

Besides hydroformylation reactions, phosphines were also used as ligands in nickel catalyzed olefin dimerization reactions. Sterically hindered phosphines bound to a catalytically active nickel center in propene dimerization reactions lead to the formation of highly branched dimers.[8] This phosphine effect first investigated in homogeneous nickel based systems was successfully transferred to biphasic ionic liquid dimerization systems by Chauvin *et al.*[9] An ionic liquid consisting of N,N'-alkylmethylimidazolium chloride mixed with aluminum chloride and ethylaluminum dichloride was applied as

cocatalyst and solvent for the catalytically active nickel complex. Ethylaluminum groups were found to suppress uncontrolled cationic olefin oligomerization reactions, which occur in solely $AlCl_3$ based ionic liquids.[10] The Institut Français du Pétrole (IFP) brought this so called DIFASOL® process to industrial application by retrofitting it to their existing homogeneous DIMERSOL® units.[11] To maintain the phosphine effect and to keep the phosphine additive in the ionic liquid, it is advantageous to introduce ionic substituents. Since chloroaluminate ionic liquids irreversibly react with any oxygen containing molecules, the ionic substituents are mainly limited to cationic pyridinium, imidazolium, ammonium, or phosphonium groups.[12]

In contrast to the $EtAlCl_2$ containing DIFASOL® system, Wasserscheid *et al.* developed a system buffered by weak organic bases.[13] Pyridine, quinoline, and pyrrole derivatives were added to slightly acidic chloroaluminate ionic liquids. The interactions of the Lewis bases with $AlCl_3$ or the $[Al_2Cl_7]^-$ species present in such liquids[14] reduced the "latent acidity"[15] preventing uncontrolled cationic olefin oligomerization reactions. The chloroaluminate ionic liquids buffered with weak organic bases were successfully employed to activate nickel complexes for dimerization reactions of 1-butene. In a recent article, Wasserscheid *et al.* extended the system to propene and 1-hexene dimerization reactions and studied the kinetics of these biphasic reactions in detail.[16]

Recently, we described the use of triphenylphosphine and triphenylbismuth as buffer for highly Lewis acidic chloroaluminate ionic liquids.[17] While triphenylbismuth already proved to be an ideal buffer, the even cheaper triphenylphosphine based systems suffered from heavy leaching of the buffer into the product phase. Thus, we decided to extend our investigations on triphenylphosphine derivatives bearing ionic substituents.

However, most of the ionic phosphines reported in the literature are of anionic nature, contain oxygen, or possess alkyl chains at the phosphorus, which is detrimental to their stability in air.[5, 12b] Wasserscheid *et al.* reported the synthesis of a triphenylphosphine derivative bearing a *para*-1,3-dimethylimidazolium moiety.[3b] Unfortunately, the synthesis was complex, and the final product could not be obtained in high purity. In this paper, we report the facile synthesis of a new cationic *para*-trimethylammonium substituted triphenylphosphine derivative (**5**, **8**). The synthesized air stable buffer and few more substituted triarylphosphines were successfully applied in nickel catalyzed propene dimerization reactions in Lewis acidic chloroaluminate ionic liquids. We also

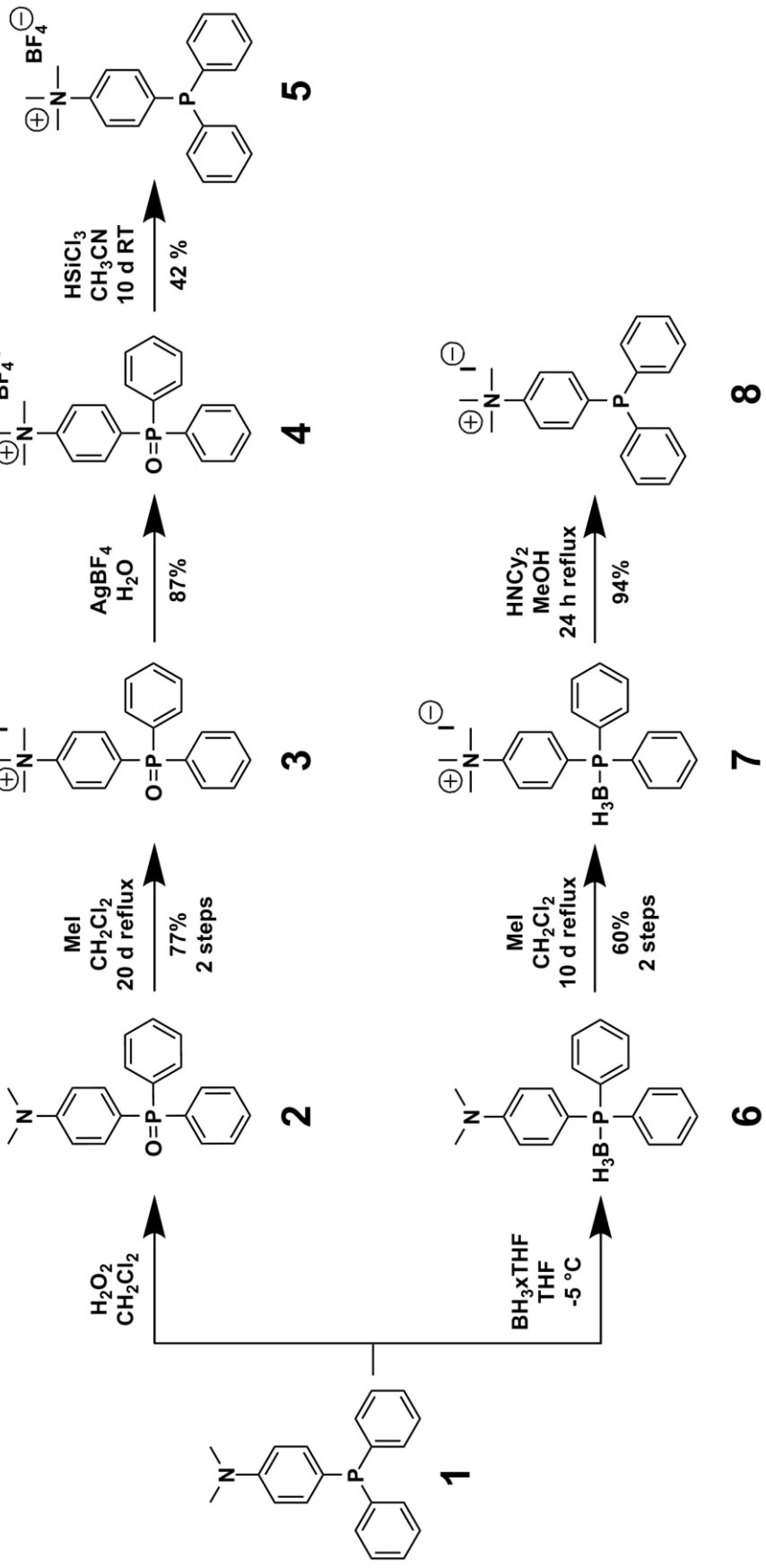
performed a ^{31}P and ^{27}Al NMR study of the interactions between the phosphorus and aluminum centers.

5.2 Results and Discussion

Synthesis of the *para*-Trimethylammonium Substituted Triphenylphosphines

In order to synthesize a compound containing both trivalent phosphorus and nitrogen centers, which is selectively alkylated at the nitrogen atom, it is necessary to introduce a protecting group at the phosphorus atom before the alkylation step. Otherwise, the more nucleophilic phosphorus atom is alkylated predominantly.[3b] The two typical ways to protect phosphorus centers are simple oxidation or the formation of a borane complex.[18]

The commercially available 4-(dimethylamino)phenyldiphenylphosphine (**1**) was converted to the corresponding phosphine oxide (**2**) quantitatively with hydrogen peroxide (**Scheme 1**). The methylated anilinium salt **3** was obtained with 77% yield from **1** after 20 days of reflux in a one pot synthesis employing the crude phosphine oxide **2**. The quaternization step using methyl iodide was slow due to the low nucleophilicity of the aniline nitrogen atom. An anion exchange reaction of the water soluble phosphine oxide **3** gave the corresponding tetrafluoroborate salt **4** with 87% yield. Removal of oxygen from a phosphine oxide is usually achieved by a reaction with excess trichlorosilane at high temperatures in presence of an amine additive.[19] By following these literature instructions, two major problems arose for compound **4**. The addition of an amine accelerator produces a hydrochloride salt, which would be difficult to get rid of in the presence of ionic products. Thus, the reaction initially was performed in refluxing acetonitrile with $HSiCl_3$ without an additional amine. After two days, the ^{31}P NMR analysis revealed that the reduction step was completed. However, the phosphorus signal appeared at δ = 20.9 ppm, which corresponded to the methylated phosphonium salt of **1**. According to the concept of hard and soft acids and bases (HSAB),[20] the soft methyl carbonium group migrated from the hard nitrogen to the soft phosphorus center.[21]



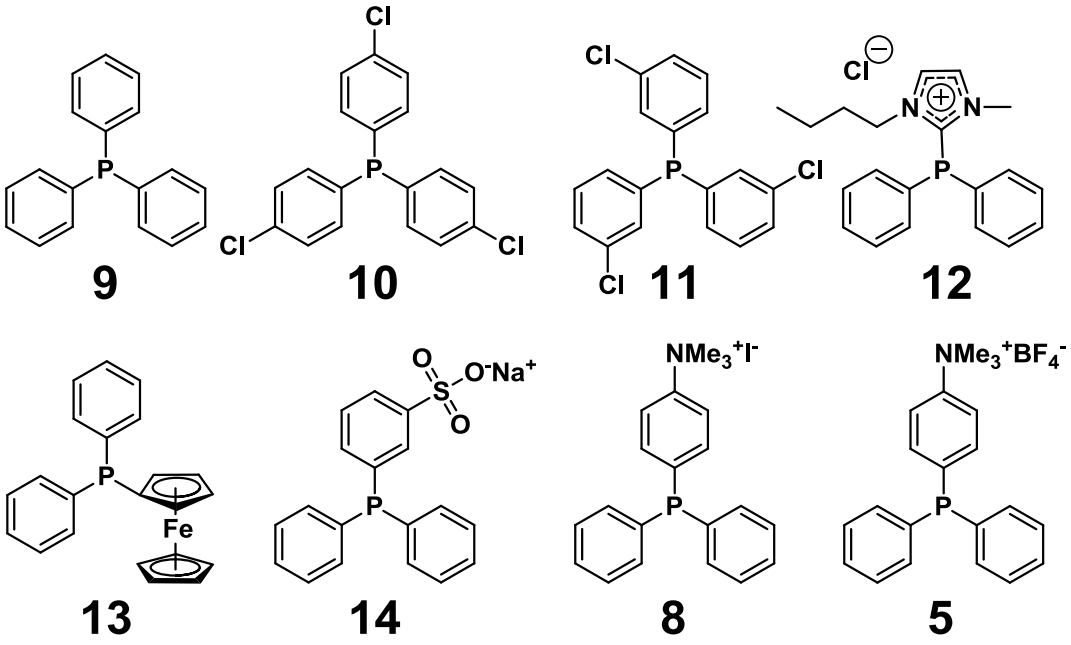
Scheme 1: Synthesis of the cationic phosphines **5** and **8**.

Thus, we performed the reaction again at ambient temperature. After ten days, the reduction was complete, and no phosphonium signal could be observed in the ^{31}P NMR spectrum. The water insoluble **5** could be extracted in 42% yield and did not rearrange at ambient temperature.

In the second route, the starting phosphine **1** was complexed with BH_3. Due to the easy product separation of the methylated borane complex **7**, which is the only CH_2Cl_2 insoluble compound within the system, the intermediate borane complex **6** did not have to be isolated. However, a small sample was purified for analysis. Compound **7** could be obtained in 60% yield in a one pot synthesis starting from **1**. The borane was removed with excess $HNCy_2$, which formed a stable and nonpolar complex with BH_3.[18] The iodide salt **8** was also insoluble in water and could be obtained in high purity. In combination with the 94% yield of the deprotection step, **8** was obtained with an overall yield of 56% from **1**.

Buffer Screening in Highly Acidic Chloroaluminate Ionic Liquids

The iodide and tetrafluoroborate salts **8** and **5** of the cationic triphenylphosphine derivative were tested towards their ability to buffer a highly acidic [1-butyl-3-methylimidazolium]$^+$[Al_2Cl_7]$^-$ ionic liquid. A composition of [buffer] / [BMIM]$^+$[Al_2Cl_7]$^-$ = 0.30 (BMIM = 1-butyl-3-methylimidazolium) was found to give good catalytic results for nickel catalyzed olefin dimerization reactions.[17] We chose to test a non coordinating counter anion like BF_4^-, which should not interact with the Lewis acidic aluminum centers, and a coordinating iodide anion. Iodide ions are softer Lewis bases compared to chlorides, but iodides do not replace chloride in [$AlCl_4$]$^-$ species. It only reacts with [Al_2Cl_7]$^-$ to give [$IAlCl_3$]$^-$ and [$AlCl_4$]$^-$ species, which slightly reduce the overall acidities of the buffered melts with increasing buffer content.[22] With the chosen buffer content of 0.30 equivalents relative to the imidazolium cation, about 0.30 equivalents of [Al_2Cl_7]$^-$ were “neutralized” to [$IAlCl_3$]$^-$ and [$AlCl_4$]$^-$. **Scheme 2** shows the triarylphospine compounds tested for their buffering ability.



Scheme 2: Triarylphosphines screened towards their buffering ability in the Lewis acidic ionic liquid $[BMIM]^+[Al_2Cl_7]^-$.

The propene dimerization reactions were carried out batchwise employing a simple bis(imino)pyridine complex of nickel(II)bromide (**15**) as the catalyst precursor.[17]

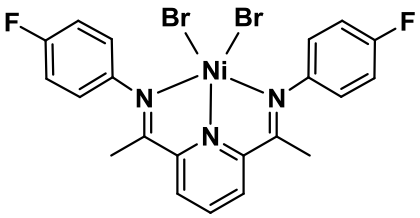


Figure 1: Catalyst precursor used for biphasic propene dimerization reactions.

Table 1 summarizes the results of the propene dimerization reactions with different buffering substances. All dimerization reactions catalyzed by complex **15** yielded a similar dimer distribution consisting of about 25% *n*-hexenes, 69% 2-methylpentenes, and 6% 2,3-dimethylbutenes (± 2%). Obviously, the ligand had no effect on the product distributions, which were similar to the distribution of a ligand free nickel salt.[16] As described in our recent publication,[17] the term “activity” was replaced by the term

"productivity". Wasserscheid *et al.* showed that above a certain concentration, the activities of the systems did not depend on the amount of catalyst anymore due to mass transport limitations.[16] Thus, the productivities can be calculated as the amount of products formed by one gram of active liquid in one hour under the assumption that the productivities of the systems do not depend on the catalyst concentration.

Table 1: Nickel catalyzed biphasic propene dimerization reactions in buffered acidic 1-butyl-3-methylimidazolium (BMIM) chloroaluminate ionic liquids.[1]

Buffer	Productivity[2]	Dimers [%]
NPh_3	> 8.6[3]	68.0
9	> 12.2[3]	57.4
10	2.9	53.5
11	6.3	78.6
12	3.7	Oil[4]
13	> 12.8[3]	69.3
14	0.4	Oil[4]
8	6.1	84.1
5	11.6	Oil[4]
$BiPh_3$	> 9.3[3]	85.5

[1] Reaction conditions: 2 – 3 g buffered ionic liquid; composition [buffer] / $[BMIM]^+[Al_2Cl_7]^-$ = 0.30; catalyst precursor 15; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Complete conversion. [4] Higher oligomers derived from a cationic oligomerization reaction.

Triphenylamine certainly coordinated too strongly to the aluminum centers resulting in a reduced buffering ability coming along with a low dimer yield of only 68%. The triphenylphosphine system lacked selectivity due to its low solubility in the ionic liquid. Most of the 0.30 buffer equivalents did not dissolve in the ionic liquid phase. Tris(*m*-chlorophenyl)phosphine (**11**) gave a higher dimer yield of 79% due to its better solubility

in the melt compared to its *para*-substituted equivalent (**10**). The 2-imidazolium-diphenylphosphine (**12**), which beared a cationic 1-butyl-3-methylimidazolium chloride moiety instead of a phenyl ring,[3b] showed no buffering ability. Only higher oligomers from uncontrolled cationic olefin oligomerization reactions initiated by the highly Lewis acidic aluminum centers were obtained.[10] In contrast, diphenylphosphinoferrocene (**13**) sufficiently buffered the system yielding 69% dimers. The addition of the sodium salt of diphenylphosphinobenzene-3-sulfonic acid (**14**) almost deactivated the system. Only small amounts of higher oligomers were formed during the reaction. Probably the oxygen of the sulfonate group reacted with chloroaluminate species deactivating the system and reducing the mobility of the buffer.

As expected, the iodide salt of the synthesized ionic phosphine **8** gave the best result of all tested phosphines providing 84% dimers. It was completely soluble in the ionic liquid and almost caught up with the $BiPh_3$ system (86% dimers[17]). However, it had to be taken into account that the additional iodide ions of the buffer reduced the overall acidity of the system, which also favoured the formation of dimers. Surprisingly, the cationic phosphine with a tetrafluoroborate anion **5** did not dissolve in the ionic liquid at all. Hence this system only produced higher oligomers.

Effects of 8 on $EtAlCl_2$ Buffered Chloroaluminate Melts

Additionally, the effect of the ionic phosphine **8** on the performance of a typical $EtAlCl_2$ buffered system was investigated (**Table 2**). For example, this composition is applied in the commercial DIFASOL® process. In batch propene dimerization reactions, the unmodified $EtAlCl_2$ buffered composition yielded about 80% dimers with catalyst precursor **15**. Addition of 0.03 equivalents of the cationic phosphine **8** slightly increased the C_6 selectivity to 84%. The addition of 0.06 equivalents of **8** resulted in 89% dimers. The combination of $EtAlCl_2$ buffered systems and an ionic phosphine buffer improved the overall dimer selectivity about 10% compared to a standard DIFASOL® system while maintaining a high productivity. Any phosphine leaching into the product phase should be prevented by its ionic character. A stable system with a high lifetime is therefore expected.

Table 2: Nickel catalyzed biphasic propene dimerization reactions in $EtAlCl_2$ buffered systems modified with the cationic phosphine **8**.[1]

[8] / [BMIMCl]	Productivity[2]	Dimers [%]
0	> 18.1[3]	79.6
0.03	> 22.5[3]	83.6
0.06	> 13.5[3]	89.1

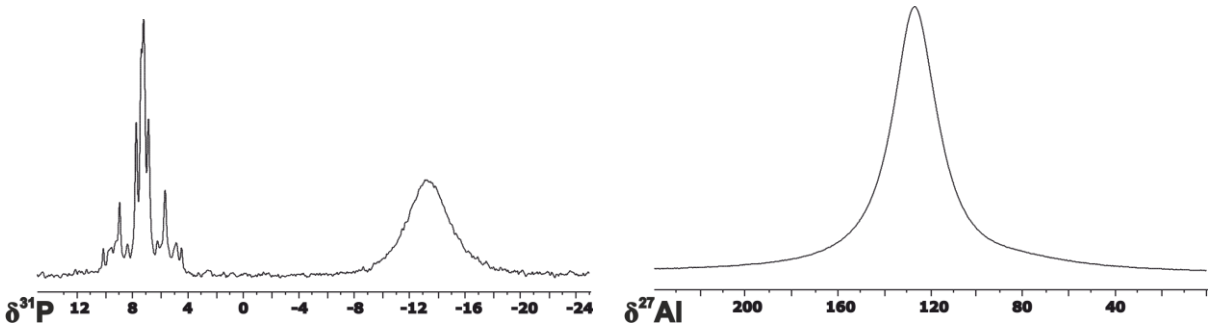
[1] Reaction conditions: 2 – 3 g buffered ionic liquid; [BMIMCl] / [$AlCl_3$] / [$EtAlCl_2$] = 1.00 / 1.20 / 0.20; catalyst precursor 15; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 45 min; 300 ml glass autoclave; 40 – 60 ml liquid propene. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Complete conversion.

NMR Investigations

Since triarylphosphines were efficient buffers for Lewis acidic chloroaluminate ionic liquids, the phosphorus center makes them predestined for ^{31}P NMR investigations. Systems with the even more effective $BiPh_3$ buffer are difficult to investigate by nuclear magnetic resonance experiments. The naturally occurring ^{209}Bi isotope displays a spin of 9/2.

First, a $[BMIM]^+[Al_2Cl_7]^-$ ionic liquid was saturated with hardly soluble PPh_3 and mixed with a few drops of C_6D_6 in an NMR tube. **Scheme 3** shows the ^{31}P and ^{27}Al NMR spectra. The “buffering” interaction can be seen clearly from the broad peak (line width at half maximum: 560 Hz) at δ = −13 ppm in the ^{31}P NMR spectrum due to fast intermolecular exchange reactions. The PPh_3 signal, which usually appears at δ = −6 ppm, is shifted to higher frequencies due to the interaction of triphenylphosphine with the Lewis acidic aluminum centers. Between δ = 4 − 10 ppm, another signal appears, which indicates a new species. It obviously consists of more than one P nuclei and gives an AB_2 spin pattern. The constitution of this compound is not clear yet.

The ^{27}Al NMR spectrum displays a line width at half maximum of 2450 Hz, which is typical for an acidic $[imidazolium]^+[Al_2Cl_7]^-$ ionic liquid.[23] Analogously to the literature, a signal with this line width arises from $[Al_2Cl_7]^-$ species. These anions are bigger than $[AlCl_4]^-$ anions and possess a less symmetrical surrounding of the Al center. Thus, the signal is broadened by efficient nuclear quadrupole relaxation.



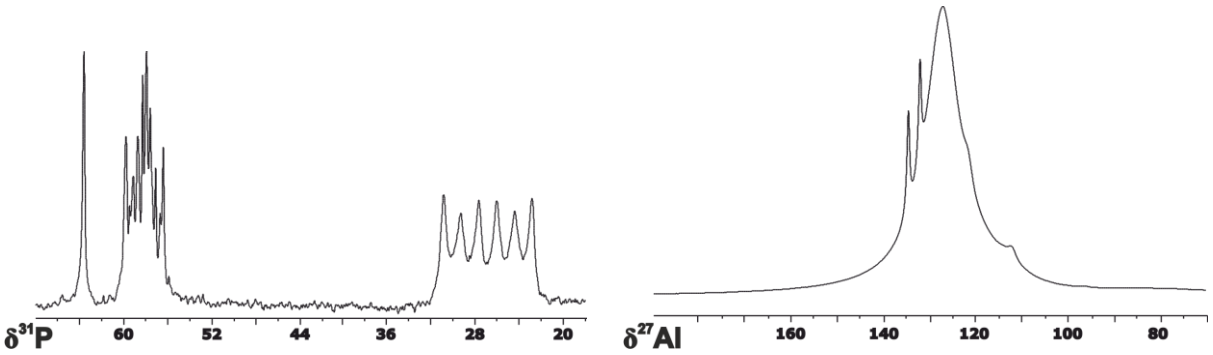
Scheme 3: ^{31}P and ^{27}Al NMR spectrum of PPh_3 in the ionic liquid $[BMIM]^+[Al_2Cl_7]^-$ (C_6D_6, 25°C).

A second sample consisting of $[BMIM]^+[Al_2Cl_7]^-$ with 0.30 equivalents of the more basic, sterically hindered tri-*tert*-butylphosphine was prepared. Surprisingly, after the addition of small amounts of C_6D_6, the system underwent a phase separation. A clear phase (**Scheme 4**) separated on top of a turbid phase (**Scheme 5**). Upon addition of more C_6D_6, the phases combined again. Both phases were investigated by means of NMR spectroscopy.

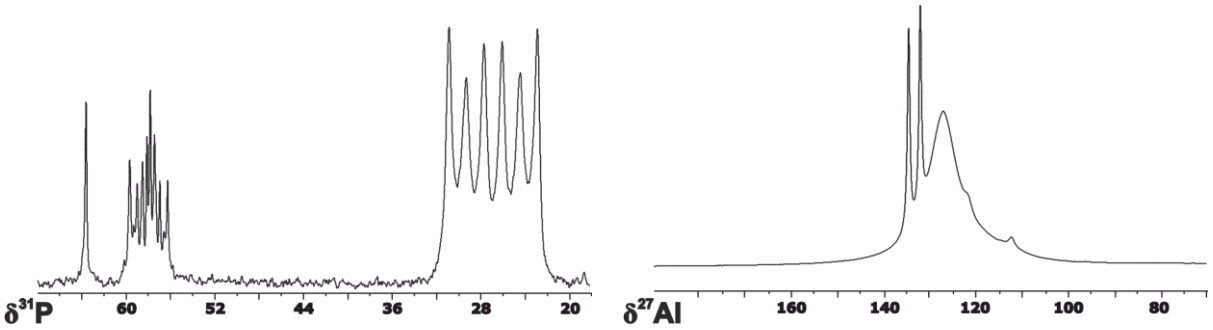
The peak at δ = 63.6 ppm belongs to excess tri-*tert*-butylphosphine, which does not interact with the ionic liquid.[24] Unlike using PPh_3, the interaction of tri-*tert*-butylphosphine with the Lewis acidic aluminum species in the ionic liquid generates an unusual sextet between δ = 22 and 32 ppm. The P–Al interaction is stronger leading to a splitting of the ^{31}P signal by the spin 5/2 nucleus ^{27}Al, and exchange reactions are slow in NMR time scale. The different intensities within the sextet are normal for couplings of 1/2 spin nuclei with a quadrupole nucleus. A simple tri-*tert*-butylphosphine adduct of $AlCl_3$ in organic solvents did not show a sextet[25] but broad signals. In toluene, the adducts of PMe_3 or PEt_3 with $AlCl_3$ only generated a singlet in the ^{31}P NMR spectrum, while a doublet was observed in the ^{27}Al NMR spectrum.[26] This could be explained with fast exchange reactions in solution. In chloroaluminate ionic liquids, the exchange rates may be reduced. The π-interactions of toluene probably reduced the Lewis acidity of $AlCl_3$ in solution leading to a weaker donor-acceptor interaction with the phosphine.

Similarly to the PPh_3 system above, the spectrum shows an AB_2 spin pattern between δ = 56 and 60 ppm. This spin system must be derived from a different phosphine species present in the liquid. Unfortunately, the nature of that species could not be determined

yet. Due to fast chlorine / alkyl exchange in the reaction mixture, ring or chain like oligophosphines could be formed. This behaviour should be discussed in another paper.



Scheme 4: ^{31}P and ^{27}Al NMR spectrum of the upper phase of the mixture $[BMIM]^+[Al_2Cl_7]^-$ / tri-*tert*-butylphosphine (0.30 equivalents) in C_6D_6 (25°C).

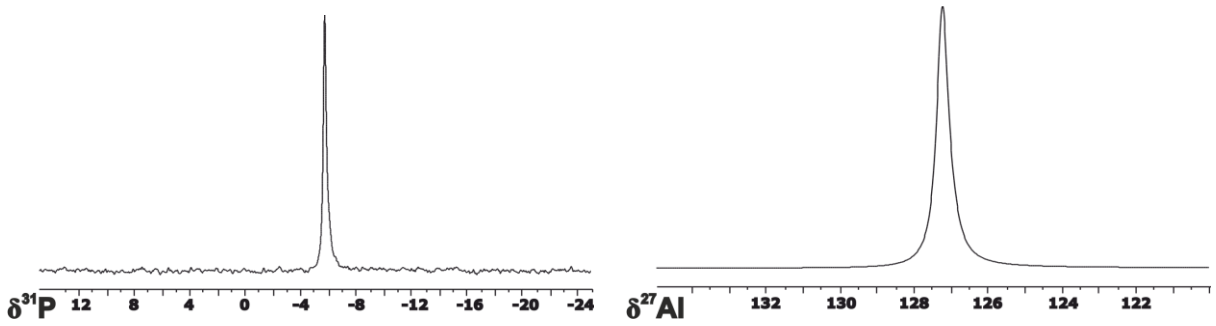


Scheme 5: ^{31}P and ^{27}Al NMR spectrum of the bottom phase of the mixture $[BMIM]^+[Al_2Cl_7]^-$ / tri-*tert*-butylphosphine (0.30 equivalents) in C_6D_6 (25°C).

The spectra of both the upper and the lower phase, display the same peak patterns. However, the concentrations are different. The P–Al interacting species is enriched in the lower phase with a ratio of approximately 83 to 17 compared to the undefined species. In the upper phase the ratio is about 55 to 45. In the ^{27}Al NMR spectra two sharp signals at δ = 134.6 and 132.1 ppm stick out of the broad overlying signal of $[Al_2Cl_7]^-$. They belong to the corresponding Al center coupling with tri-*tert*-butylphosphine. The signals of at least two other Al species must be present in the system indicated by two shoulders at about 112 and 122 ppm.

For comparison, another sample was prepared by dissolving the ionic phosphine **8** in a neutral $[BMIM]^+[AlCl_4]^-$ ionic liquid (**Scheme 6**). The ^{31}P NMR signal appears at δ = −5.7

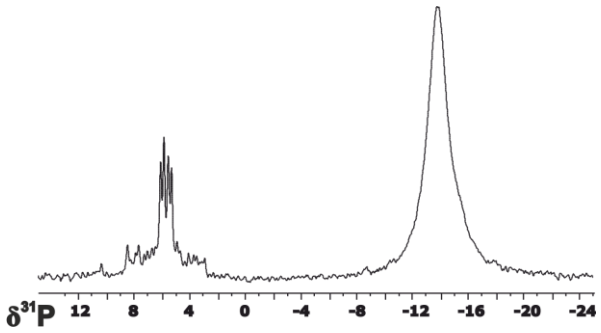
ppm with a line width at half maximum of 32 Hz. These signals are broader than those obtained from **8** dissolved in $CDCl_3$ (2.2 Hz). The line width of 41 Hz in the ^{27}Al NMR spectrum also correlates with a typical line width of 23 Hz measured for neutral imidazolium based chloroaluminate ionic liquids.[23a] Thus, there is only little interaction of the phosphorus atoms with the $[AlCl_4]^-$ species.



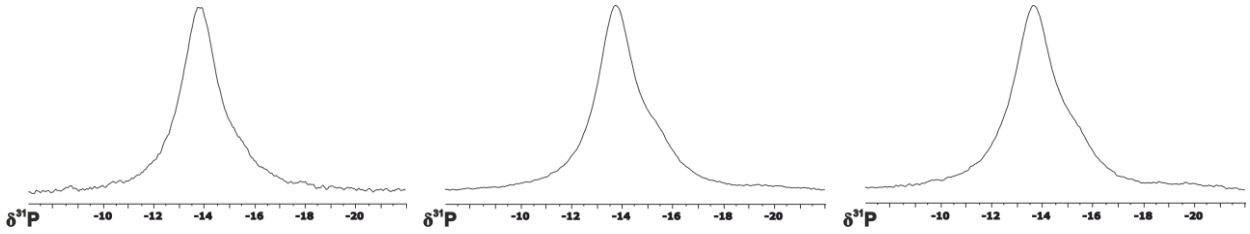
Scheme 6: ^{31}P and ^{27}Al NMR spectra of the cationic phosphine **8** in the ionic liquid $[BMIM]^+[AlCl_4]^-$ (C_6D_6, 25°C).

Finally, three samples of the cationic phosphine **8** in $[BMIM]^+[Al_2Cl_7]^-$ with concentrations of 0.10 (**Scheme 7**), 0.30 and 0.50 equivalents (**Scheme 8**) were prepared and investigated by NMR spectroscopy. In the ^{31}P NMR spectra, the signal derived from the P–Al interaction appears at δ = 13.8 ppm in all three samples. The multiplet of the undefined phosphine species was observed between δ = 3 and 9 ppm. With increasing phosphine content, a shoulder develops in the ^{31}P NMR signal induced by additional iodide anions coming along with the addition of the ionic phosphine.

Our results showed that weak P–Al interactions are crucial for phosphine buffered Lewis acidic chloroaluminate ionic liquid cocatalysts. The strong Lewis base tri-*tert*-butylphosphine coupled with aluminum to give a doublet in the ^{27}Al NMR and a sextet in the ^{31}P NMR spectrum. In contrast, only broad signals were observed for triarylphosphine buffers. A highly dynamic system is obtained from the combination of weakly Lewis basic triarylphosphines in combination with Lewis acidic chloroaluminate melts. The fast P–Al exchange is necessary to maintain a sufficient Lewis acidity to activate nickel catalyst precursor as well as to suppress uncontrolled cationic olefin oligomerization reactions.



Scheme 7: ^{31}P NMR spectrum of 0.10 equivalents of the cationic phosphine **8** in the ionic liquid $[BMIM]^+[Al_2Cl_7]^-$ (C_6D_6, 25°C).



Scheme 8: Excerpts of the ^{31}P NMR spectra of the mixtures containing 0.10 (left), 0.30 (middle) and 0.50 (right) equivalents of the cationic phosphine **8** in the ionic liquid $[BMIM]^+[Al_2Cl_7]^-$ (C_6D_6, 25°C).

Conclusions

The synthesized cationic triphenylphosphine derivative **8** successfully buffered the highly Lewis acidic $[BMIM]^+[Al_2Cl_7]^-$ ionic liquid. Its tetrafluoroborate equivalent **5** was insoluble in the ionic liquid. A nickel complex could be activated with the buffered composition and dimerized propene in a biphasic reaction with a selectivity of 84% to give dimers. Undesired uncontrolled cationic olefin oligomerization reactions were prevented by the addition of 0.30 equivalents of **8** to the ionic liquid. Adding 0.06 equivalents of **8** to a commercially used DIFASOL® ionic liquid composition, the dimer yield could be increased from 80% to 89%. The P–Al interaction was investigated by ^{31}P and ^{27}Al NMR spectroscopy. While no P–Al coupling between buffering triarylphosphines and aluminum centers could be observed, the more basic but sterically hindered tri-*tert*-butylphosphine coupled with ^{27}Al to give an expected but unusual sextet in the ^{31}P NMR spectrum. The straight-forward synthesis of the cationic phosphine **8** in combination

with the high yield makes such cationic triphenylphosphine derivatives interesting for biphasic reactions. When triphenylphosphine is replaced by its cationic derivative, leaching effects can be minimized and catalyst lifetimes should increase. Due to the absence of acidic protons, triphenylphosphines with quaternized ammonium substituents can also be applied when highly reactive metal alkyl groups like alkylaluminum bonds are present. Besides dimerization and polymerization reactions, possible applications can be found in biphasic hydroformylation,[27] hydrogenation,[6b] or cross coupling reactions.[4]

5.3 Experimental Section

General Remarks

All chemical manipulations were carried out using standard Schlenk techniques under argon atmosphere. THF was distilled from Na/K alloy. CH_2Cl_2 was distilled in two steps from P_4O_{10} and CaH_2. For drying methanol, magnesium turnings were dissolved in the solvent before distillation. Demineralized water was degassed with argon prior to use. Acetonitrile (Acros, p.a.) was used as received. ^{1}H, ^{11}B, ^{13}C, ^{27}Al and ^{31}P NMR spectra were recorded on Varian Inova 300 MHz or 400 MHz spectrometers. Chemical shifts are given relative to Me_4Si: δ ^{1}H ($CHCl_3$) = 7.24 ppm; δ ^{1}H ($CD_3(SO)CD_2H$) = 2.50 ppm; δ ^{13}C ($CDCl_3$) = 77.2 ppm; δ ^{13}C ($CD_3(SO)CD_3$) = 39.5 ppm; external 85% H_3PO_4 [δ ^{31}P = 0 ppm for Ξ (^{31}P) = 40.480747 MHz]; external 1.1 M $Al(NO_3)_3$ in D_2O [δ ^{27}Al = 0 ppm for Ξ (^{27}Al) = 26.056890 MHz]; external BF_3-OEt_2 [δ ^{11}B = 0 ppm for Ξ (^{11}B) = 32.083971 MHz]. Chemical shifts are given to ± 0.1 ppm in ^{13}C and ^{31}P NMR spectra and ± 0.4 ppm in ^{11}B and ^{27}Al NMR spectra. The products of the dimerization experiments were characterized by gas chromatography (Agilent 6850). GC-MS spectra were measured on a Thermo Scientific FOCUS DSQ™. Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70 eV). Elemental analyses were performed with a VarioEl III CHN instrument. Acetanilide was used as a standard. Propene (99.3%) was purchased from Riessner Gase, Lichtenfels, and was dried over a column packed with P_4O_{10}. $EtAlCl_2$ (0.9 M in heptane) and tri-*tert*-butylphosphine (95%) were purchased from Acros and used without further purification. Compound **11** was synthesized according to the literature.[4a] Triphenylamine, triphenyl-

phosphine, triphenylbismuth, tris(*p*-chlorophenyl)phosphine, and tris(*m*-chlorophenyl)-phosphine were purchased from ABCR. 1-Butyl-3-methylimidazolium chloride, dicyclohexylamin, trichlorosilane, *p*-(dimethylamino)phenyldiphenylphosphine, the borane-tetrahydrofurane complex, $AlCl_3$ (ReagentPlus®), and compound **13** were purchased from Sigma-Aldrich and used without further purification. Diphenylphosphinoferrocene was obtained from MCAT.

Synthesis of the Ionic Liquids

The ionic liquids were synthesized by directly mixing the corresponding amounts of $AlCl_3$ and chloride salt in a cooled Schlenk tube. In the case of $EtAlCl_2$ containing systems, a 0.9 molar solution of $EtAlCl_2$ in heptane was added to the liquid, and the solvent was removed in vacuo. The obtained ionic liquids were stored in Schlenk tubes.

Procedure for the Dimerization Reactions using Buffered Ionic Liquids

Prior to the experiments, about 2 ml of the ionic liquid were filled into a Schlenk tube and mixed with the buffer. After the buffer had dissolved upon stirring, the nickel complex **15** was added. The obtained homogeneous solution was syringed into the reaction vessel. Its amount was determined by the weight difference of the syringe. In the case of partly soluble buffers, the mixture was stirred until the solid was distributed homogeneously in the liquid. Then, the slurry was syringed into the reaction vessel.

For all dimerization experiments, a 300 ml glass autoclave equipped with a stirring bar and a magnetic stirrer with a stirring rate of 1200 min^{-1} was used. The glass autoclave was kept in a drying oven at 150°C for several hours before an experiment. After addition of the active ionic liquid, propene (40 to 60 ml) was condensed into the glass autoclave by liquid nitrogen cooling. Then, the autoclave was placed in a metal box for safety reasons, and the temperature was regulated by an external water bath. After the experiment, the pressure was slowly released by opening a valve. The product fraction was filtered through a short plug of silica and analyzed by gas chromatography.

Synthesis of [4-(Trimethylammonium)phenyldiphenylphosphine Oxide] Iodide 3

Hydrogen peroxide (5.0 g, 30% in H_2O) was slowly added to a solution of **1** (11.11 g, 36.38 mmol) in CH_2Cl_2 (100 ml). The mixture was stirred for 30 minutes and evaporated to dryness. The crude phosphine oxide **2** was dissolved in CH_2Cl_2 (100 ml) followed by

the addition of methyl iodide (15 ml, 241 mmol). After refluxing the mixture for 20 days, the white precipitate was filtered off. Washing three times with CH_2Cl_2 followed by vacuum drying yielded **3** (yield: 12.95 g, 77%).

Compound **3**: White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm)=8.24 (dd, J=1.5, 8.9 Hz, 2H), 7.84 (dd, J=9.1Hz, J=10.9 Hz,2H), 7.39 – 7.62 (m, 10H), 3.99 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm)=149.7 (d, C, J=3.1 Hz), 136.7 (d, C, J=100 Hz), 134.6 (d, 2CH, J=10.5 Hz), 132.8 (d, 2CH, J=2.7 Hz), 132.1 (d, 4CH, J=10.1 Hz), 131.1 (d, 2C, J=106 Hz), 129.1 (d, 4CH, J=12.4 Hz), 121.2 (d, 2CH, J=11.9 Hz), 58.0 (s, $3CH_3$). ^{31}P NMR (120 MHz, $CDCl_3$): δ=28.2 ppm.

EI-MS data: 321 M –MeI (100), 244 M –MeI –Ph (22).

Synthesis of [4-(Trimethylammonium)phenyldiphenylphosphine Oxide] Tetrafluoroborate 4

To a solution of **3** (2.03 g, 4.38 mmol) in water (20 ml), 8.75 ml of an aqueous $AgBF_4$ solution (4.38 mmol, 0.5 N) were added. The precipitated AgI was filtered off and washed three times with small amounts of water. Evaporation of the solution yielded **4** (yield: 1.61 g, 87%).

Compound **4**: White solid; ^{1}H NMR (300 MHz, DMSO-d_6): δ(ppm)=8.14 (d, J=8.4 Hz, 2H), 7.90 (dd, J=8.7 Hz , J=10.7 Hz, 2H), 7.54 – 7.72 (m, 10H), 3.62 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6): δ(ppm)=149.7 (d, C, J=3.1 Hz), 135.2 (d, C, J=100 Hz), 133.2 (d, 2CH, J=10.5 Hz), 132.5 (d, 2CH, J=1.9 Hz), 131.8 (d, 2C, J=104 Hz), 131.5 (d, 4CH, J=10.0 Hz), 129.0 (d, 4CH, J=12.0 Hz), 121.2 (d, 2CH, J=11.9 Hz), 56.3 (s, $3CH_3$). ^{31}P NMR (120 MHz, DMSO-d_6): δ=25.2 ppm. ^{11}B NMR (96 MHz, DMSO-d_6): δ=–1.2 ppm.

EI-MS data: 321 M –BF_4 –Me (100), 244 M –BF_4 –Me –Ph (25).

Synthesis of [4-(Trimethylammonium)phenyldiphenylphosphine] Tetrafluoroborate 5

To a suspension of **4** (3.52 g, 8.32 mmol) in CH_3CN (50 ml), trichlorosilane (6.0 ml, 59 mmol) was added slowly. After the addition, the initially insoluble **4** dissolved. The homogeneous solution was stirred for 10 days at ambient temperature. The precipitate was filtered off, and the filtrate was evaporated to dryness. Water (10 ml) was added,

and the mixture was stirred for two hours. Then, the suspension was concentrated in vacuum and cooled to 0°C. Filtration yielded the water insoluble **5** (yield: 1.41 g, 42%).

Compound **5**: White solid; ^{1}H NMR (300 MHz, DMSO-d_6): δ(ppm)=7.98 (d, J=8.3 Hz, 2H), 7.37 – 7.48 (m, 8H), 7.24 – 7.33 (m, 4H), 3.59 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6): δ(ppm)=147.4 (C), 139.9 (d, C, J=15.3 Hz), 135.5 (d, 2CH, J=10.7 Hz), 134.3 (d, 2C, J=19.6 Hz), 133.4 (d, 4CH, J=20.0 Hz), 129.5 (2CH), 129.0 (d, 4CH, J=7.2 Hz), 120.9 (d, 2CH, J=6.4 Hz), 56.3 (s, 3CH_3). ^{31}P NMR (120 MHz, DMSO-d_6): δ=–6.9 ppm. ^{11}B NMR (96 MHz, DMSO-d_6): δ=–1.2 ppm.

EI-MS data: 320 M –BF_4 (15), 305 M –BF_4 –Me (100).

Synthesis of [4-(Trimethylammonium)phenyldiphenylphosphine-Borane] Iodide 7

A solution of **1** (11.90 g, 39.0 mmol) in THF (150 ml) was cooled to –5°C. Then, the borane-THF adduct (46.8 ml, 1 N in THF) was added, and the solution was stirred for two hours at 0°C. A small sample of the white precipitate was withdrawn and washed with THF for analysis of the intermediate product **6**. After warming up to ambient temperature, the solvent of the remaining mixture was removed in vacuo, and the residue was dissolved in 200 ml CH_2Cl_2. Subsequently, methyl iodide (15 ml, 241 mmol) was added, and the solution was refluxed for ten days. Filtration and washing with methylene chloride gave **7** (yield: 11.90 g, 60%), which proved to be insoluble in CH_2Cl_2.

Compound **6**: White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm)=7.49 – 7.60 (m, 4H), 7.33 – 7.49 (m, 8H), 6.69 (dd, J=2.0, 9.0 Hz, 2H), 2.98 (s, 9H), 0.5 – 2.0 (br, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm)=152.2 (d, C, J=2.0 Hz), 134.7 (d, 2CH, J=10.8 Hz), 133.1 (d, 4CH, J=9.7 Hz), 130.9 (2CH), 130.8 (d, C, J=58 Hz), 128.7 (d, 4CH, J=10.1 Hz), 113.0 (d, 2C, J=67 Hz), 111.9 (d, 2CH, J=10.7 Hz), 40.1 (s, 3CH_3). ^{31}P NMR (120 MHz, $CDCl_3$): δ=19.3 ppm (br d, J=58 Hz). ^{11}B NMR (96 MHz, $CDCl_3$): δ=–37.6 ppm (br).

EI-MS data: 319 $M^{\bullet+}$ (6), 305 M –BH_3 (100).

Compound **7**: White solid; ^{1}H NMR (300 MHz, DMSO-d_6): δ(ppm)=8.16 (dd, 2H, J=1.5, 9.2 Hz), 7.52 – 7.77 (m, 12H), 3.63 (s, 9H), 0.5 – 2.0 (br, 3H).

^{13}C NMR (75 MHz, DMSO-d_6): δ(ppm)=149.4 (d, C, J=2.4 Hz), 134.2 (d, 2CH, J=10.4 Hz), 132.7 (d, 4CH, J=9.9 Hz), 132.1 (d, 2CH, J=2.6 Hz), 131.5 (d, C, J=56 Hz), 129.4 (d, 4CH, J=10.2 Hz), 127.4 (d, 2C, J=58 Hz), 121.7 (d, 2CH, J=10.2 Hz), 56.3 (s, 3CH_3). ^{31}P NMR (120 MHz, DMSO-d_6): δ=20.4 ppm (br). ^{11}B NMR (96 MHz, DMSO-d_6): δ=–37.2 ppm (br).

EI-MS data: 319 M –MeI (8), 305 M –MeI –BH_3 (100).

Synthesis of [4-(Trimethylammonium)phenyldiphenylphosphine] Iodide 8

Dicyclohexylamine (18 ml, 90 mmol) was added to a solution of **7** (10.30 g, 22.3 mmol) in methanol (200 ml). After refluxing for ten hours, a white precipitate formed. The precipitate was washed three times with ethyl acetate/*n*-hexane (1/1), three times with water and once again with ethyl acetate/*n*-hexane. The washing procedure was supported by the use of an ultrasonic bath once for each solvent. Vacuum drying yielded **8** in high purity (yield: 9.37 g, 94%).

Compound **8**: White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.87 (d, J=8.7 Hz, 2H), 7.42 (dd, J=6.0 Hz, J=8.7 Hz, 2H), 7.22 – 7.35 (m, 10H), 3.97 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm)=147.2 (C), 142.9 (d, C, J=17.0 Hz), 135.5 (d, 2CH, J=19.2 Hz), 135.4 (d, 2C, J=10.3 Hz), 134.1 (d, 4CH, J=20.3 Hz), 129.7 (2CH), 129.1 (d, 4CH, J=7.4 Hz), 120.0 (d, 2CH, J=6.1 Hz), 58.0 (s, 3CH_3). ^{31}P NMR (160 MHz, $CDCl_3$): δ=–5.2 ppm.

EI-MS data: 320 M –I^- (4), 305 M –MeI (100).

Elemental analysis (calculated, found for $C_{21}H_{23}INP$): C (56.39, 56.45), H (5.18, 5.02), N (3.13, 3.19).

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6 Nickel Catalyzed Propene Dimerization Reactions in $BiPh_3$ Buffered Chloroaluminate Ionic Liquids: High Performance with Unconventional Cations

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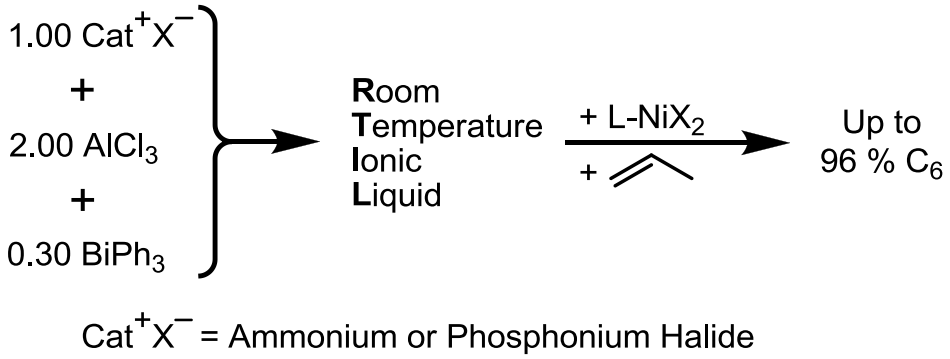


Abstract: The addition of triphenylbismuth efficiently buffers Lewis acidic chloroaluminate ionic liquids over a wide range of compositions. Since the melting points of these ternary mixtures are lower compared to unbuffered chloroaluminate systems, the scope of cations for the formation of buffered room temperature ionic liquids is greatly extended. The buffered ionic liquids were used to activate nickel complexes for selective biphasic propene dimerization reactions. Lifetimes, selectivities and productivities of such dimerization catalysts could be adjusted by the choice of the cation and

the composition. At lower reaction temperatures, the selectivities to give dimers increased significantly. Propene dimers were obtained with selectivities of up to 98%. A cation screening with 100 ammonium and phosphonium halide salts was performed. N-Methylpyrrolidine hydrochloride gave the best results in terms of selectivity and lifetime. Propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts were catalyzed by various soluble nickel compounds with similar performances. The introduction of basic, sterically demanding tricyclohexylphosphine ligands led to higher degrees of branching, however, at the expense of lower dimer selectivities.

6.1 Introduction

Selective dimerization reactions of α-olefins attracted a lot of attention in the second half of the 20th century, after Ziegler described the “nickel effect” in 1955.[1] Nickel impurities from previous hydrogenation reactions were found to catalyze selective ethene dimerization reactions to give butenes in the presence of alkylaluminum compounds. Ziegler was originally interested in chain growth and polymerization reactions. However, his discovery also launched an intensive research on selective nickel catalyzed dimerization reactions of short chain olefins in the following decades.[2]

The DIMERSOL® process of the Institut Français du Pétrole (IFP) is the largest industrial process based on nickel complexes activated by alkylaluminum cocatalysts. It was developed by Chauvin *et al.* in the 1970s[3] to dimerize propene (DIMERSOL® G) or 1-butene (DIMERSOL® X) selectively. Currently, 35 licensed DIMERSOL® units with typical capacities between 20000 and 90000 tons per year are in use for selective dimerization reactions of short chain olefins.[4]

About 30 years ago, Wilkes *et al.* and Osteryoung *et al.* reported the first room temperature ionic liquids based on aluminum chloride.[5] In the 1980s, these chloro-aluminate ionic liquids were thoroughly investigated in terms of their physical and electrochemical properties.[6] It took about ten more years until chloroaluminate ionic liquids started to attract attention as new media for biphasic catalysis.[7]

Initially, Lewis acidic chloroaluminate melts were used as catalysts for Friedel Crafts alkylation reactions.[8] In the 1990s, Chauvin *et al.* developed nickel catalyzed biphasic

dimerization reactions of α-olefins in organochloroaluminate ionic liquids.[9] Ethylaluminum groups were found to suppress uncontrolled cationic olefin oligomerization reactions, which occur in solely $AlCl_3$ based ionic liquids.[10] The IFP brought this so called DIFASOL® process to industrial application by retrofitting it to their existing DIMERSOL® units.[4a, 11]

Besides alkylaluminum groups, the addition of weak Lewis bases also reduces the "latent acidity"[12] of chloroaluminate melts. While Wasserscheid *et al.* used pyrrole, pyridine, and quinoline derivatives to prevent undesired cationic olefin oligomerization reactions,[13] we recently reported that triphenylphosphine and triphenylbismuth efficiently buffer even highly acidic chloroaluminate ionic liquids.[14] These buffered chloroaluminate melts were successfully employed to activate nickel complexes for selective propene dimerization reactions.

Buffering with Lewis base additives is advantageous compared to the commercial DIFASOL® system. First, buffering with $EtAlCl_2$ is restricted to only slightly acidic compositions. If higher acidities are chosen, the dimer selectivities decrease. Second, at higher alkylaluminum contents, leaching of neutral chloroalkylaluminum compounds formed by disproportionation reactions[15] becomes a major problem.[11b] Also, alkylaluminum cocatalysts contribute to the deactivation of Ni(II) catalysts by reducing Ni(II) to its zero oxidation state.[16] Usually, the melting points of aluminum chloride based ionic liquids display a minimum for highly acidic melts, while a local maximum is observed around equimolar compositions.[6a, 17] Therefore, DIFASOL® systems are limited to cations intrinsically forming low melting liquids, e.g. N,N'-alkylmethylimidazolium or N-alkylpyridinium salts.[13b]

In a recent paper, we described that the melting points of acidic chloroaluminate systems are reduced upon addition of $BiPh_3$. Thus, it was possible to obtain buffered room temperature ionic liquid compositions from aluminum chloride and cations, which would only yield solids at ambient temperature without $BiPh_3$.[14a] Furthermore, the scope of potential cations became even larger since low melting highly acidic systems could be used for nickel catalyzed selective olefin dimerization reactions. Because no reactive alkylaluminum groups were present in $BiPh_3$ buffered chloroaluminate ionic liquids, these systems were not limited to quaternary ammonium cations. Instead,

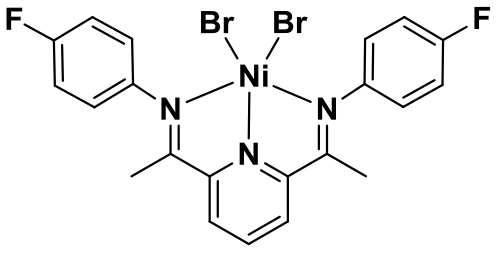
cheap halide salts like amine hydrochlorides could be used, which can be recovered easily upon hydrolysis.

In this paper, we report nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts with 100 mostly unconventional cation compositions. Only two out of 100 mixtures did not form liquids at ambient temperature. Furthermore, the effect of Lewis acidities, buffer contents and reaction temperatures on the dimer selectivities was investigated. Finally, several nickel complexes were tested for their performances in $BiPh_3$ buffered chloroaluminate melts.

6.2 Results and Discussion

Variation of Buffering and Acidity Levels

As described in our recent paper, not only slightly acidic chloroaluminate melts could be buffered with $BiPh_3$ but also highly acidic $[cation]^+[Al_2Cl_7]^-$ systems.[14a] Therefore, the effect of different acidities and $BiPh_3$ contents in chloroaluminate ionic liquids on nickel catalyzed propene dimerization reactions was investigated in detail (**Table 1**). For the screening experiments, we used our standard nickel complex **A** as the catalyst precursor (**Figure 1**).



A

Figure 1: Catalyst precursor used for biphasic propene dimerization reactions.

We chose a system based on the commercially available 1-butyl-3-methylimidazolium (BMIM) tetrachloroaluminate, to which the corresponding amounts of $AlCl_3$ were added. With slightly acidic $AlCl_3$ / BMIMCl = 1.20 systems, which were used by Wasserscheid *et al.*[13b] and for DIFASOL® systems[9c], dimers were obtained starting with 0.07

equivalents of $BiPh_3$ (2). With increasing buffer content, selectivities increased. Employing 0.30 equivalents of $BiPh_3$, already 96% dimers were obtained (4), however, at the expense of a reduced productivity.

Table 1: Nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts with different compositions.[1]

No.	$[AlCl_3]$ / [BMIMCl]	$[BiPh_3]$ / [BMIMCl]	Productivity[2]	C_6 [%]
1	1.20	0.05	> 15.8[3]	Oil[4]
2	1.20	0.07	> 10.8[3]	89.2
3	1.20	0.12	> 8.0[3]	93.1
4	1.20	0.30	6.7	96.0
5	1.30	0.12	> 8.0[3]	81.8
6	1.50	0.12	> 10.6[3]	74.1
7	1.50	0.18	> 12.0[3]	83.2
8	2.00	0.12	> 11.4[3]	74.8
9	2.00	0.18	> 12.3[3]	79.5
10	2.00	0.24	> 7.4[3]	83.3
11	2.00	0.30	> 9.3[3]	85.5
12	2.00	0.60	> 11.5[3]	90.6

[1] Reaction conditions: 2.5 – 3.5 g buffered ionic liquid; catalyst precursor A; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 70 ml liquid propene. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Complete conversion. [4] Higher oligomers derived from a cationic oligomerization reaction.

Due to mass transfer limitations,[13d] the term “activity” was replaced by “productivity”. Thus, above a catalyst concentration of about 10^{-6} mol / $g_{ionic\ liquid}$,[14a] the product yield per hour is proportional to the amount of ionic liquid and independent from the catalyst

concentration. As expected, increasing acidities with a constant buffer level reduced the dimer selectivities. However, from an $AlCl_3$ / BMIMCl ratio of 1.50 to 2.00, the selectivities dropped only a few percent if the buffer level was held constant. Thus, the advantage of low melting points at highly acidic compositions did not have to be paid by disproportional high amounts of buffer. With only 0.12 equivalents of buffer, the maximum acidic system still yielded about 75% dimers (8).

Cation Screening

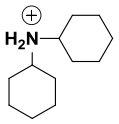
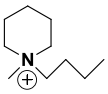
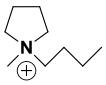
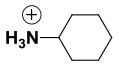
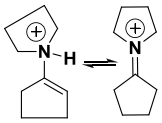
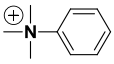
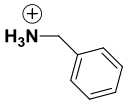
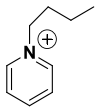
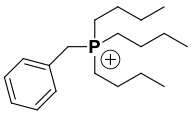
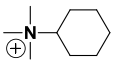
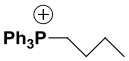
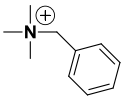
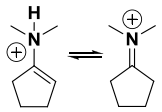
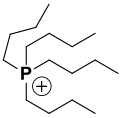
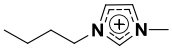
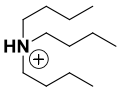
Considering these results, we were curious if our system can be extended to rather unusual and cheap cations. In the literature, only a few chloroaluminate systems were mentioned, which did not rely on standard imidazolium or pyridinium cations. Trimethylammonium heptachlorodialuminate was used for cationic oligomerization reactions of 1-decene.[18] The use of triethylamine hydrochloride, dibutylamine hydrochloride, ethylamine hydrochloride, and dimethylamine hydrochloride was reported for Friedel Crafts alkylation reactions.[7e] Dimethylaniline hydrochloride,[19] and several quaternary asymmetric benzyl substituted melts were described, too.[20] However, none of these were used for nickel catalyzed olefin dimerization reactions due to the above mentioned melting point and acidity restrictions. Friedel Crafts alkylation reactions or cationic olefin oligomerization reactions employ the Lewis acidic ionic liquid itself as catalyst. Thus, in these cases a variation of the cation should only result in minor changes on the results of the reactions. In contrast, the performances of nickel catalyzed olefin dimerization reactions in $BiPh_3$ buffered chloroaluminate melts should strongly depend on the cation. The reactions are catalyzed by a nickel complex, not by the ionic liquid itself. It is necessary that the $BiPh_3$ buffer dissolves well in the ionic liquids to minimize leaching effects. Also, the cation determines the viscosities and the solubilities of the substrate olefin within the ionic liquids. Both the viscosity and the solubility of the substrate are crucial since biphasic nickel catalyzed dimerization reactions in chloroaluminate melts suffer from a mass transport limitation of the olefin.[13d] Therefore, we decided to perform a systematic screening of cations including quaternary ammonium salts, hydrochlorides of primary, secondary and tertiary amines, phosphonium salts, heterocyclic ammonium salts, and cations with more than one heteroatom. One hundred different halide salts and their $AlCl_3$ / halide salt = 2.00 compositions were synthesized. These compositions were buffered with 0.30

equivalents of $BiPh_3$ and tested for nickel catalyzed propene dimerization reactions. The screening reactions were performed in batch experiments. Furthermore, the lifetime of each system was investigated qualitatively. After each experiment, the product phase was decanted until the dimer selectivity dropped significantly. In **Table 2**, 33 selected cations and the corresponding C_6 selectivities obtained in the first batch experiment are shown. The complete dataset can be found in the Supporting Information.

Since the reference complex **A** had no effect on the branching of the hexene dimers,[14a] all C_6 fractions consisted of (± 2%) 25% *n*-hexenes, 69% 2-methylpentenes, and 6% 2,3-dimethylbutenes. This correlated to the typical product distribution obtained from ligand free nickel salts.[13d] Because the productivities of such buffered systems mainly depended on the buffering level,[14a] the productivities of different cations should not be compared directly. Cations yielding compositions with a good $BiPh_3$ efficiency automatically displayed higher dimer selectivities and subsequently lower productivities. Therefore, the goal was to identify systems, which kept high selectivities over many repetitions.

Surprisingly, 95 of 100 compositions produced dimers. Only two cations, formamidine hydrochloride and 1,4-diazabicyclo[2.2.2]octane hydrochloride, yielded solids at ambient temperature (see Supporting Information). Even the pentavalent triphenylphosphine dichloride based system (45) successfully dimerized propene to give 50% dimers (45). However, the systems displayed big differences in their overall performances. The best results were obtained with quaternary ammonium salts and hydrochlorides of tertiary amines. In general, hydrochlorides of primary and secondary amines were less selective. However, even small changes on the cation could have severe effects on the lifetimes and selectivities of the systems. For example, the 1-butyl-3-methylimidazolium chloride cation, which was used for the initial acidity screening experiments, was found among the worst quaternary ammonium cations (22). Introduction of an ethyl (17) instead the butyl chain significantly improved the selectivity as well as the lifetime of the system (see Supporting Information). As already reported, the system based on N-methylpyrrolidine hydrochloride (26) displayed the best performance in terms of selectivity and qualitative lifetime.[14a] In the case of the $BiPh_3$ buffer, there appears to be an optimum range of carbon atoms for ammonium salts, roughly between five and nine. Ionic liquids derived from cations with more or less carbon atoms dropped much faster in terms of selectivity than those within that range.

Table 2: Selected results of the cation screening for nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts (left: quaternary ammonium chloride salts; middle: hydrochlorides of tertiary amines; right: hydrochlorides of primary and secondary amines and phosphonium salts).[1]

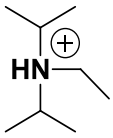
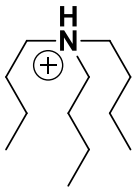
No.	Cation	C_6 [%]	No.	Cation	C_6 [%]	No.	Cation	C_6 [%]
13		92.0	24		93.1	35		90.4
14		91.2	25		92.5	36		83.0
15		90.9	26		91.6	37		79.0
16		90.1	27		90.7	38		76.1
17		90.0	28		90.0	39		73.3
18		89.7	29		89.9	40		66.1
19		89.3	30		89.6	41		92.5
20		89.3	31		89.6	42		91.0
21		89.2	32		89.6	43		85.4
22		86.2	33		89.4	44		68.6
23		75.9	34		89.1	45		49.5

[1] Reaction conditions: 2.5 – 4.0 g buffered ionic liquid; composition $[BiPh_3]$ / $[cation]^+[Al_2Cl_7]^-$ = 0.30; catalyst precursor A; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene.

Temperature Effect on Dimer Selectivities

Further, we investigated the effect of the reaction temperature on dimer selectivities with 0.30 and 0.60 equivalents of $BiPh_3$ (**Table 3**). The reactions were performed either at ambient temperature or at 0°C.

Table 3: Nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts at 0°C and 25°C.[1]

Cation	No.	[Buffer] / [Cation]	Temperature [°C]	Productivity[2]	C_6 [%]
	46	0.30	25	> 10.1[3]	90.7
	47	0.30	0	> 6.7[3]	95.5
	48	0.60	25	4.6	93.8
	49	0.60	0	–[4]	–
	50	0.30	25	> 10.6[3]	89.4
	51	0.30	0	> 12.9[3]	96.0
	52	0.60	25	> 7.6[3]	90.8
	53	0.60	0	1.8	98.0

[1] Reaction conditions: 3.2 – 5.2 g buffered ionic liquid; composition $[BiPh_3]$ / $[cation]^+[Al_2Cl_7]^-$ = 0.30; catalyst precursor A; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; stirring rate = 1200 min^{-1}; t = 60 min for T = 25°C; t = 120 min for T = 0°C; 300 ml glass autoclave; 40 – 60 ml liquid propene. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Complete conversion. [4] Composition solid at 0°C.

While the selectivity of an ethyldiisopropylamine (Hunig's base) hydrochloride based system with 0.30 equivalents of $BiPh_3$ increased from 91% at 25°C (46) to 96% at 0°C (47) the mixture containing 0.60 equivalents of $BiPh_3$ solidified at 0°C (49). Thus, the series was repeated with tributylamine hydrochloride. By lowering the temperature to 0°C, the dimer selectivity could be increased by 7% to 96% (51) and 98% (53), respectively. The experiments also showed that above a certain buffer concentration, the addition of more $BiPh_3$ only resulted in minor improvements of the dimer selectivity.

Thus, a cation screening was mandatory to identify halide salts, which display high lifetimes combined with high selectivities.

Effect of Different Nickel Catalyst Precursors on Dimer Selectivities

So far, only catalyst precursor **A** was used as a reference in all screening experiments. Now, a series of typical nickel(II) halides and complexes was tested for their performances in combination with $BiPh_3$ buffered chloroaluminate melts (**Table 4**). Considering the results of our previous cation screening, N-methylpyrrolidine hydrochloride mixed with two equivalents of aluminum chloride and buffered with 0.30 equivalents of $BiPh_3$ was chosen as reference system.

Since propene dimerization reactions in buffered chloroaluminate melts are limited by mass transfer of the olefin,[13d] the productivities of all nickel compounds should be the same if a sufficiently high catalyst concentration was chosen. In a recent paper, we determined the minimum catalyst concentration necessary to exclude catalyst concentration restrictions to be around 10^{-6} mol_{Ni} / $g_{ionic\ liquid}$.[14a] We applied a concentration of 10^{-5} mol_{Ni} / $g_{ionic\ liquid}$ to ensure that the catalyst concentration was not the rate determining factor.

First, the four binary nickel halides were tested. All of them yielded very high selectivities of more than 90%. However, the productivities were quite different. Nickel fluoride produced 24.9 g product per gram buffered ionic liquid (54). The other halides displayed lower productivities. This behaviour might be explained by the low solubility of these ligand free halide salts. Although 10^{-5} mol_{Ni} / $g_{ionic\ liquid}$ were added to the liquid, the salts did not dissolve completely. Nickel chloride seemed to be almost insoluble in the buffered liquid. The bromide and iodide salts did not dissolve very well, too. Thus, the amount of catalyst, which had actually dissolved in the ionic liquid, might have been below 10^{-6} mol_{Ni} / $g_{ionic\ liquid}$. In this case, not only the mass transfer of the olefin but also the catalyst concentration determined the productivity.

To prove this theory, the triphenylphosphine adducts of nickel chloride and nickel bromide were tested, too (58, 59). Indeed, both complexes readily dissolved in the ionic liquid and yielded almost the same productivity of around 28 $g_{product}$ / $g_{ionic\ liquid}$ x h with a selectivity around 91% to give C_6. The productivities of nickel hexafluoroacetylacetonate (60) and bis-(N-isopropylsalicylaldimine)-nickel(II) (61) were only slightly lower.

The compositions of all C_6 fractions were consistent with ligand free nickel salts. Hydrogenation showed that the hexenes consisted of 25% *n*-hexenes, 69% 2-methylpentenes, and 6% 2,3-dimethylbutenes (± 2%). Either, the triphenylphosphine ligands were abstracted from the Lewis acidic ionic liquids, or they did not influence the degree of branching.

Table 4: Catalyst screening for nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts.[1]

No.	Catalyst Precursor	C_6 [%]	Conversion [%]	Productivity[2]
54	NiF_2	90.9	69	24.9
55	$NiCl_2$	95.4	7	2.5
56	$NiBr_2$	92.6	43	14.7
57	NiI_2	93.0	47	16.1
58	$(PPh_3)_2NiCl_2$	90.8	80	28.8
59	$(PPh_3)_2NiBr_2$	91.0	81	28.2
60	$Ni(hfacac)_2$	91.8	75	23.1
61	NiL_2[3]	90.6	75	27.0

[1] Reaction conditions: 4.4 g buffered ionic liquid; composition $[BiPh_3]$ / $[N\text{-methylpyrrolidinium}]^+[Al_2Cl_7]^-$ = 0.30; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 40°C; stirring rate = 600 min^{-1}; t = 60 min; stirred 300 ml Parr stainless steel autoclave; 130 – 160 g liquid propene; hfacac = hexafluoroacetylacetonate. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] NiL_2 = bis-(N-isopropylsalicylaldimine)-Ni(II)).

Effect of Tricyclohexylphosphine Ligands on the Dimer Structure

Finally, nickel chloride complexed by two sterically demanding tricyclohexylphosphine ligands was employed as catalyst precursor for olefin dimerization reactions in $BiPh_3$ buffered chloroaluminate ionic liquids (**Table 5**). Sterically hindered phosphines bound to a catalytically active nickel center in propene dimerization reactions are known to favour the formation of highly branched dimers.[2c, 2e, 2f] Especially 2,3-dimethylbutenes

are interesting due to their high research octane number (RON). They can be used as octane booster to increase the RON of low octane motor fuel.[2d]

Table 5: Effect of tricyclohexylphosphine on the degree of branching in nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts.[1]

No.	Catalyst Precursor	[$BiPh_3$] / [Cation]	C_6 [%]	HEX [%]	MP [%]	DMB [%]	Productivity[2]
62	A	0.30	93.7	25	69	6	18.5
63	$(PCy_3)_2NiCl_2$	0.30	78.5	16	54	30	26.3
64	$(PCy_3)_2NiCl_2$	0.60	83.9	13	48	39	13.3

[1] Reaction conditions: 3.5 – 4.4 g buffered ionic liquid; composition [$AlCl_3$] / [N-methylpyrrolidine x HCl] = 2.00; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 40°C; stirring rate = 600 min^{-1}; t = 60 min; stirred 300 ml Parr stainless steel autoclave; 250 ml liquid propene; HEX = *n*-hexenes; MP = 2-methylpentenes; DMB = 2,3-dimethylbutenes. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h.

Indeed, the tricyclohexylphosphine ligands increased the 2,3-dimethylbutene (DMB) content from 6% to 30% applying the same buffer level of 0.30 equivalents triphenylbismuth. However, the overall dimer selectivity dropped from more than 90% to 79% if tricyclohexylphosphine ligands were present (63). With 0.60 equivalents of $BiPh_3$, the DMB yield could be increased to 39%. The higher buffer level also increased the dimer selectivity slightly to 84%.

Conclusion

We have shown that $BiPh_3$ efficiently buffered Lewis acidic chloroaluminate melts over a wide range of compositions. The ratio between cation, aluminum chloride, and $BiPh_3$ can be tuned to obtain tailor-made dimerization systems. Lifetimes, selectivities, and productivities can be adjusted by the choice of the cation and the composition. The addition of triphenylbismuth reduced the melting points of the resulting chloroaluminate mixtures and thus, allowed the use of almost any ammonium or phosphonium halide cation. By performing a cation screening with 100 halide salts, we found that N-methylpyrrolidine hydrochloride gave the best catalytic results in terms of selectivity and

lifetime. We further showed that olefin dimerization reactions in buffered chloroaluminate melts can be catalyzed by various nickel compounds with similar performances. The introduction of basic, sterically demanding tricyclohexylphosphine ligands led to higher degrees of branching, however, at the expense of lower dimer selectivities.

Supporting Information Available

Experimental procedures, the preparation of halide salts and ionic liquids are described in the Supporting Information. The results of the cation screening experiments are also listed in detail.

Acknowledgements

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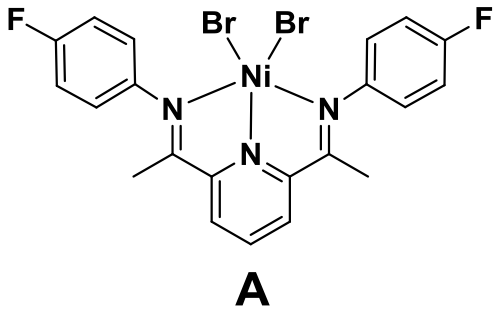
6.4 Supporting Information

6.4.1 Experimental Section

General Remarks

All chemical manipulations were carried out using standard Schlenk techniques under argon atmosphere. The products of the dimerization experiments were characterized by gas chromatography (Agilent 6850) and GC-MS (FOCUS DSQ™ Thermo Scientific). Propene (99.3%) was purchased from Riessner Gase, Lichtenfels, and was dried over a column packed with P_4O_{10}. Triphenylbismuth was purchased from ABCR and used without further purification. 1-Butyl-3-methylimidazolium tetrachloroaluminate (BASF), $AlCl_3$ (ReagentPlus®), $Ni(hfacac)_2$, $(PPh_3)_2NiCl_2$, $(PPh_3)_2NiBr_2$, $(PCy_3)_2NiCl_2$, and all nickel halides were purchased from Sigma-Aldrich and used as received. Complex **A**[1] and bis-(N-isopropylsalicylaldimine)-Ni(II)) were synthesized according to a literature procedure.[2]



A

Figure 1: Catalyst precursor used for biphasic propene dimerization reactions.

Synthesis of Buffered Ionic Liquid Catalyst Compositions

The ionic liquids were synthesized by directly mixing the corresponding amount of $AlCl_3$ and halide salt in a cooled Schlenk tube. In the case of BMIM based liquids, $AlCl_3$ was added to commercial 1-butyl-3-methylimidazolium tetrachloroaluminate. Few ml of an ionic liquid were filled into another Schlenk tube, and the corresponding amount of $BiPh_3$ was dissolved in the liquid by stirring. After the nickel catalyst precursor had been

added, the homogeneous solution was syringed into the reaction vessel. Its amount was determined by the weight difference of the syringe.

Procedure for Biphasic Propene Dimerization Reactions

For the Lewis acidity, cation, and temperature screening experiments, a 300 ml glass autoclave equipped with a stirring bar and a magnetic stirrer with a stirring rate of 1200 min^{-1} was used. The glass autoclave was kept in a drying oven at 150°C for several hours before an experiment. After the addition of the active ionic liquid, propene (40 to 60 ml) was condensed into the glass autoclave by liquid nitrogen cooling. Then, the autoclave was placed in a metal box for safety reasons, and the temperature was regulated by an external water bath. After the experiment, the pressure was slowly released by opening a valve. The product fraction was filtered through a short plug of silica and analyzed by gas chromatography.

For the catalyst screening experiments, a stirred 300 ml Parr stainless steel autoclave was used. The steel vessel was kept in a drying oven at 150°C for several hours before an experiment, and it was filled with argon. The catalyst containing vessel was evacuated, and liquid propene (200 ml) was soaked into it at 77 K. The reaction was started by quickly heating the vessel to 40°C with boiling water. Cooling of the highly exothermic reaction was achieved manually by an external liquid nitrogen cooled acetone bath. After the experiment, the vessel was cooled to 0°C, and the pressure was slowly released. After reaching ambient temperature, the weight difference of the vessel was determined, and the product phase was analyzed by gas chromatography. To determine the content of *n*-hexenes, 2-methylpentenes, and 2,3-dimethylbutenes, the product fraction was hydrogenated with palladium on activated carbon and analyzed by gas chromatography.

6.4.2 Cation Synthesis

All purchased ammonium salts were dried under reduced pressure at elevated temperatures prior to use.

Quaternary Ammonium Salts

Trimethylhexadecylammonium chloride (1), N,N,N',N'-tetramethylformamidinium chloride (6), 1-butyl-4-methylpyridinium chloride (11), benzyltrimethylammonium chloride

(24), methyltributylammonium chloride (27), methyltrioctylammonium chloride (34), tetramethylammonium chloride (35), and N,N-dimethylmethyleneiminium chloride (36) were purchased from Sigma-Aldrich. 1-Ethyl-3-methylimidazolium chloride (17), trimethylphenylammonium chloride (19), hexamethylguanidinium chloride (29), and dichloromethylene-dimethyliminium chloride (32) were purchased from Acros. Chloroethane (Chloraethyl, Dr. Henning) was purchased in a local pharmacy. The free amine precursors and haloalkanes used to synthesize the cations described below were purchased from Sigma-Aldrich, Acros, or ABCR.

N-Benzylpyridinium chloride (2), 1-benzyl-3-methylimidazolium chloride (8), N-benzyl-N-methylpyrrolidinium chloride (10), tributylbenzylammonium chloride (14), dimethylcyclohexylbenzylammonium chloride (20), dimethyldibenzylammonium chloride (25), and dimethylethylbenzylammonium (26) chloride were synthesized following the literature procedure for 1-benzyl-3-methylimidazolium chloride (8).[3]

Trimethylethylammonium chloride (15), N,N-dimethylpyrrolidinium chloride (16), trimethylcyclohexylammonium chloride (23), N-methylpyridinium chloride (28), and N,N-dimethylpiperidinium chloride (30) were obtained in a one step reaction by chloromethylation of the corresponding tertiary amines with methylchloroformate in almost quantitative yield applying literature procedures.[4]

N-Propyl-N-methylpyrrolidinium chloride (4), N-butyl-N-methylpyrrolidinium chloride (9), N-hexyl-N-methylpyrrolidinium chloride (18), and N-butyl-N-methylpiperidinium chloride (7) were synthesized following the literature procedure for N-butyl-N-methylpyrrolidinium chloride (9).[5]

N-Ethyl-N-methylpyrrolidinium (3) chloride and dimethylethylcyclohexylammonium chloride (12) were obtained as white precipitates from reactions of the corresponding amines with three equivalents of chloroethane in toluene at 70°C. The reactions were performed in a pressure Schlenk tube with a reaction time of ten days.

6-Azoniaspiro[5.5]undecane bromide[6] (33), 5-azoniaspiro[4.4]nonane bromide[6] (21), dimethylethylphenylammonium bromide[7] (26), 1,4-bis(3-methylimidazolium-1-yl)butane chloride[8] (13), dimethylbenzylphenylammonium chloride[9] (37), and N-butylpyridinium chloride[10] (22) were synthesized following literature procedures.

Hydrochlorides of Primary and Secondary Amines

Ethylamine hydrochloride (40), dimethylamine hydrochloride (42), acetamidine hydrochloride (44), benzylamine hydrochloride (45), methylamine hydrochloride (48), aniline hydrochloride (49), and formamidine hydrochloride (51) were purchased from Sigma-Aldrich. Guanidine hydrochloride (50) was purchased from ABCR. The free amine precursors used to synthesize the cations described below were purchased from Sigma-Aldrich, Acros, or ABCR.

Dicyclohexylamine hydrochloride (38), pyrrolidine hydrochloride (39), cyclohexylamine hydrochloride (41), dibenzylamine hydrochloride (43), methylbenzylamine hydrochloride (46), and N,N,N′,N′-tetramethylguanidine hydrochloride (47) were synthesized by slowly adding concentrated aqueous hydrochloric acid to a cooled flask containing the corresponding amines. Optionally, several hydrochlorides could be precipitated by the addition of isopropanol or acetone to the concentrated aqueous solution. All other compounds were obtained by vacuum drying of the aqueous solution at elevated temperatures.

Hydrochlorides of Tertiary Amines

1-(2-Chloroethyl)piperidine hydrochloride (53), triethylamine hydrochloride (57), trimethylamine hydrochloride (71), 1-methylimidazolium chloride (86), imidazole hydrochloride (88), and pyridine hydrochloride (91) were purchased from Sigma-Aldrich. The commercially available amine precursors and haloalkanes used to synthesize the cations described below were purchased from Sigma-Aldrich, Acros, or ABCR.

N-Propylpyrrolidine, N-isopropylpyrrolidine, N-*n*butylpyrrolidine, N-*tert*-butylpyrrolidine, N-cyclohexylpyrrolidine, and N-propylpiperidine were obtained from the corresponding primary amines and dibromoalkanes applying the literature procedure described for N-*tert*-butylpyrrolidine.[11] N,N-Dimethyl-1-cyclopenten-1-amine was synthesized according to the literature.[12]

N-Methylpyrrolidine hydrochloride (61), N-ethylpyrrolidine hydrochloride (70), N-propylpyrrolidine hydrochloride (75), N-isopropylpyrrolidine hydrochloride (65), N-*n*butylpyrrolidine hydrochloride (78), N-*tert*-butylpyrrolidine hydrochloride (52), N-cyclohexylpyrrolidine hydrochloride (85), N-methylpiperidine hydrochloride (69), N-ethylpiperidine hydrochloride (77), N-propylpiperidine hydrochloride (60), N-cyclohexylpiperidine hydro-

chloride (81), dimethylethylamine hydrochloride (68), methyldiethylamine hydrochloride (55), dimethylisopropylamine hydrochloride (56), ethyldiisopropylamine hydrochloride (64), tributylamine hydrochloride (76), triisobutylamine hydrochloride (63), triisopentylamine hydrochloride (79), trioctylamine hydrochloride (59), dimethylcyclohexylamine hydrochloride (83), diethylcyclohexylamine hydrochloride (80), methyldicyclohexylamine hydrochloride (82), ethyldicyclohexylamine hydrochloride (73), dimethylbenzylamine hydrochloride (84), tribenzylamine hydrochloride (89), 1,2,2,6,6-pentamethylpiperidine hydrochloride (87), and 1,4-diazabicyclo[2.2.2]octane hydrochloride (92) were synthesized by slowly adding concentrated aqueous hydrochloric acid to a cooled flask containing the corresponding amines. Optionally, several hydrochlorides could be precipitated by the addition of isopropanol or acetone to the concentrated aqueous solution. All other compounds were obtained by vacuum drying of the aqueous solution at elevated temperatures.

2-Methyl-1-pyrroline hydrochloride (66), 1-pyrrolidino-1-cyclopentene hydrochloride (67), 1-piperidino-1-cyclohexene hydrochloride (74), N,N-dimethyl-1-cyclopenten-1-amine hydrochloride (72), and N,N-dimethylaniline hydrochloride (90) could not be obtained as solids from aqueous solution and were prepared from their free amines and HCl gas in diethylether following the literature procedure described for triphenylphosphine hydrochloride[13] (99).

N-Benzylpyrrolidine hydrochloride (62) and N-benzylpiperidine hydrochloride (58) were synthesized directly from benzyl chloride and pyrrolidine or piperidine following the literature procedure for 1-benzyl-3-methylimidazolium chloride[3] (8).

Phosphonium Salts

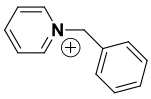
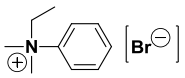
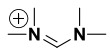
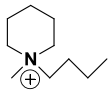
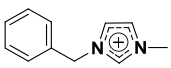
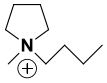
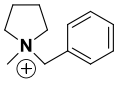
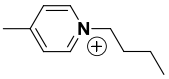
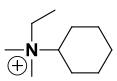
Trihexyltetradecylphosphonium chloride (93), butyltriphenylphosphonium chloride (95), tetrabutylphosphonium chloride (97), tetraphenylphosphonium chloride (98), and triphenylphosphine dichloride (100) were purchased from ABCR.

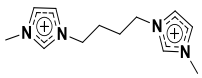
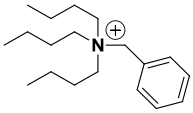
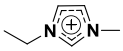
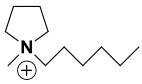
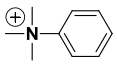
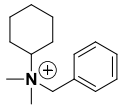
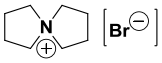
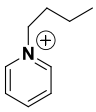
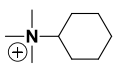
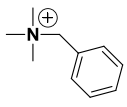
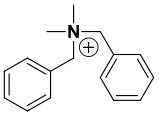
Benzyltributylphoshonium chloride (94) and benzyltriphenylphosphonium chloride (96) were synthesized from the corresponding tertiary phosphine and benzyl chloride following the literature procedure for 1-benzyl-3-methylimidazolium chloride[3] (8). Triphenylphosphine hydrochloride was synthesized according to the literature[13] (99).

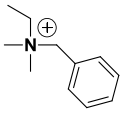
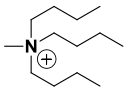
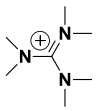
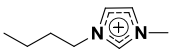
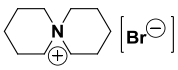
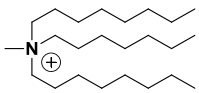
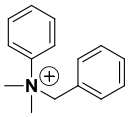
6.4.3 Cation Screening

Quaternary Ammonium Salts

Table 1: Cation screening for nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts (sorted in descending order of selectivities in run 1).[1]

No.	Cation	Run 1 C_6 [%] Prod.[2]	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
1		95.1 6.0	93.5 7.3	87.6 > 10.1	70.2 9.5	69.3 8.9	62.5 7.5					
2		92.3 8.9	91.9 9.7	91.9 > 10.5	89.9 > 11.1	76.9 > 12.0	61.3 7.8	Oil 7.0				
3		92.0 7.8	92.1 9.0	90.2 9.2	88.0 > 11.7	80.5 > 10.5	65.4 7.9	61.9 7.1				
4		91.6 > 13.1	89.6 > 12.3	87.2 > 14.0	71.8 > 11.4	61.9 9.0	56.2 7.3					
5		91.5 > 12.4	89.7 > 12.1	86.2 > 14.1	76.4 > 11.4	74.5 > 11.5	74.0 11.2	77.6 9.0	77.7 8.7	77.2 6.4	68.3 5.9	
6		91.4 9.0	80.3 > 15.2	69.5 > 11.2	67.2 9.1	67.2 7.5	63.8 6.8					
7		91.2 > 10.8	89.7 > 11.4	86.5 > 10.9	83.7 > 10.6	75.3 > 10.6	70.8 8.9	69.6 6.9				
8		90.9 > 9.4	89.5 > 10.7	88.0 > 12.2	75.9 > 11.2	65.6 9.7	59.5 7.4	Oil 6.8				
9		90.9 > 11.7	91.4 > 10.8	91.7 > 11.2	91.6 9.9	91.1 > 10.9	90.3 > 11.3	89.0 > 10.2	86.0 > 11.4	78.5 > 10.7	70.9 8.8	71.1 8.4
10		90.9 > 8.7	92.3 > 10.4	91.9 > 9.3	92.0 > 9.2	91.8 > 9.8	89.4 > 9.4	89.1 > 11.7	80.0 > 11.0	73.5 7.7		
11		90.7 > 11.9	87.9 > 10.5	86.7 > 11.9	76.6 > 11.5	60.0 9.3						
12		90.7 > 13.4	88.9 > 14.1	82.5 > 14.2	67.4 > 14.0	65.3 10.9	62.8 9.7					

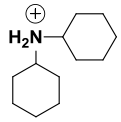
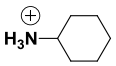
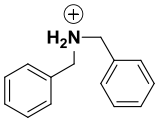
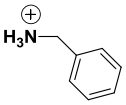
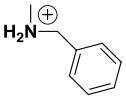
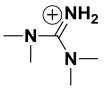
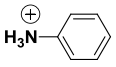
No.	Cation	Run 1 C_6 [%] Prod.[2]	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
13		90.5 8.9	89.9 8.3	90.1 10.4	89.1 9.4	86.7 12.7	77.4 > 14.5	72.3 9.1	62.6 6.1			
14		90.3 > 9.5	90.0 > 11.3	86.0 > 13.6	73.6 > 13.1	72.3 8.8	69.3 6.4	65.2 5.4				
15		90.3 7.0	91.9 7.6	91.9 7.1	91.8 9.1	89.9 > 10.1	74.9 > 10.4	71.2 8.8	66.7 5.4			
16		90.1 10.3	89.8 10.4	89.1 > 11.5	89.0 > 11.6	71.7 > 11.6	63.2 9.2					
17		90.0 > 9.9	89.4 > 9.1	90.9 > 10.8	89.3 > 8.7	89.5 > 9.9	88.8 > 9.6	86.5 > 9.6	84.0 > 9.4	67.8 7.7	64.6 8.8	
18		89.9 > 11.6	89.2 > 13.3	83.0 > 14.2	63.0 10.8	60.2 9.9						
19		89.7 > 13.0	89.9 > 14.3	88.8 > 14.4	85.9 > 12.7	77.8 > 14.5	75.4 > 14.0	74.0 7.6	66.9 4.6			
20		89.6 > 7.8	90.1 > 8.9	86.0 > 10.1	79.7 > 9.2	65.1 > 7.6	72.8 > 7.7	55.5 5.1				
21		89.6 8.1	91.5 8.4	92.0 9.4	92.2 8.9	92.4 9.2	91.7 9.6	90.8 9.6	90.2 > 10.7	86.8 > 11.1	78.4 > 10.2	77.9 5.5
22		89.3 > 11.5	86.4 > 11.9	85.1 > 12.6	81.8 > 13.4	58.0 8.5	55.9 8.0					
23		89.3 > 9.0	91.3 > 9.5	92.2 > 10.5	91.5 > 10.7	91.0 > 10.1	90.9 > 10.9	89.3 > 10.0	84.3 > 12.9	77.2 > 11.0	74.2 8.9	Oil 7.7
24		89.2 > 11.5	86.6 > 12.6	84.9 > 12.8	75.4 > 12.9	64.5 8.8						
25		89.0 8.3	84.1 > 10.6	77.3 8.1	59.1 8.8							

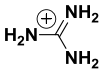
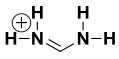
No.	Cation	Run 1 C_6 [%] Prod.[2]	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
26		88.9 > 10.6	89.1 > 10.9	78.2 > 11.9	63.5 > 10.1							
27		88.6 > 9.3	84.3 > 9.0	81.0 > 11.2	64.0 > 9.0							
28		88.0 > 9.6	87.9 > 9.5	87.2 > 10.1	85.9 > 10.7	83.5 > 10.8	80.4 > 11.7	74.1 > 10.4	71.4 > 10.6	70.1 > 9.72	69.0 > 8.7	64.2 7.4
29		87.3 8.0	69.3 7.5	73.8 7.2	66.5 9.7							
30		86.7 > 10.8	87.6 > 10.4	86.1 > 10.7	86.3 > 10.0	85.3 > 10.7	85.3 > 11.7	82.3 > 11.6	70.2 > 9.3	69.3 8.3		
31		86.2 > 10.2	85.8 > 11.2	81.4 > 12.2	68.7 > 12.6	63.5 9.0						
32		85.1 6.8	82.6 7.8	73.7 > 10.3	70.2 > 9.5	67.1 8.1	65.7 5.3					
33		84.9 > 7.8	87.2 > 9.1	87.2 > 9.4	88.1 > 10.3	88.0 > 9.7	87.2 > 9.2	86.6 > 10.4	83.6 > 10.1	79.7 > 10.4	76.5 > 8.3	75.4 7.1
34		80.3 > 10.0	55.9 4.7									
35		75.9 > 9.0	70.1 > 11.9	70.9 > 9.8	71.3 > 8.7	70.6 > 7.9	70.8 8.8	64.4 6.1				
36		50.5 9.5	Oil 8.6									
37		Oil (decomp.) 7.3										

[1] Reaction conditions: 2.5 – 4.0 g buffered ionic liquid; composition $[BiPh_3]$ / $[cation]^+[Al_2Cl_6X]^-$ = 0.30 (X = Cl, Br); chloride salts if not otherwise mentioned; catalyst precursor A; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene; products decanted after each run; > = complete conversion; Oil = only higher oligomers. [2] Productivity given in $g_{product}$ / $g_{ionic\ liquid}$ x h.

Hydrochlorides of Primary and Secondary Amines

Table 2: Cation screening for nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts (sorted in descending order of selectivities in run 1).[1]

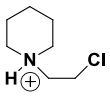
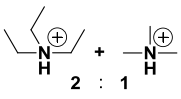
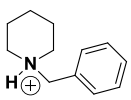
No.	Cation	Run 1 C_6 [%] Prod.[2]	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
38		90.4 > 9.1	88.5 > 8.2	88.5 9.9	70.4 > 11.5	66.5 > 9.9	63.4 6.7			
39		83.0 3.1	84.1 4.1	78.5 5.2	70.0 8.5	69.9 6.5	65.0 5.0			
40		79.0 6.0	79.3 5.9	74.1 > 9.5	65.2 > 9.7	67.4 6.8	71.5 6.5	67.5 5.4	67.3 3.3	
41		76.1 > 8.8	72.6 > 10.8	70.2 > 10.0	70.1 > 9.3	62.0 8.6				
42		73.3 > 7.9	71.5 > 7.8	76.6 > 7.9	69.5 > 7.7	68.1 > 8.1	60.7 > 8.4	65.6 > 8.1	66.5 > 7.1	69.2 5.8
43		73.0 > 9.6	65.0 > 10.6	61.3 > 9.2						
44		67.7 > 10.1	62.3 > 8.4	60.4 8.3	57.0 5.9	Oil 5.4				
45		66.1 > 9.8	68.1 > 9.9	72.1 7.6	69.5 6.3	69.3 4.6	49.7 4.5	Oil 3.9		
46		64.3 > 13.8	63.6 > 12.1	Oil > 9.9						
47		60.9 > 9.8								
48		59.7 > 12.8	68.0 > 13.1	67.2 > 12.1	72.6 > 13.5	73.5 11.1	73.4 5.9	62.1 4.7		
49		Oil 6.8								

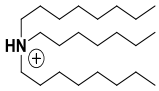
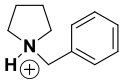
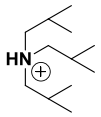
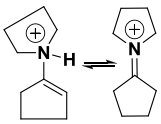
No.	Cation	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
		C_6 [%]								
		Prod.[2]								
50		Oil 6.5								
51		Buffered IL solid								

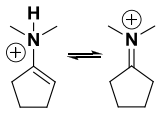
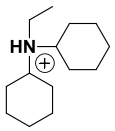
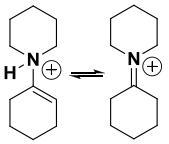
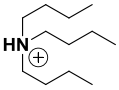
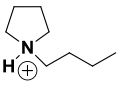
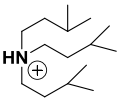
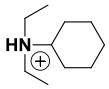
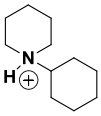
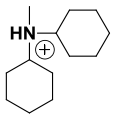
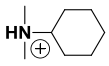
[1] Reaction conditions: 2.5 – 4.0 g buffered ionic liquid; composition $[BiPh_3]$ / $[cation]^+[Al_2Cl_7]^-$ = 0.30; catalyst precursor A; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene; products decanted after each run; > = complete conversion; Oil = only higher oligomers. [2] Productivity given in $g_{product}$ / $g_{ionic\ liquid}$ x h.

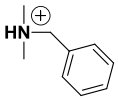
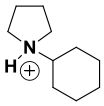
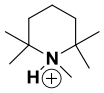
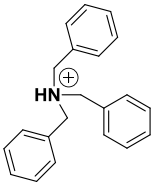
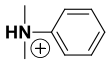
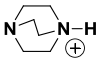
Hydrochlorides of Tertiary Amines

Table 3: Cation screening for nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts (sorted in descending order of selectivities in run 1).[1]

No.	Cation	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
		C_6 [%]										
		Prod.[2]										
52		93.1 7.4	93.6 8.3	94.1 7.5	92.0 8.1	78.0 > 10.5	69.6 8.8	56.7 7.4				
53		93.1 7.8	93.3 8.2	92.9 9.5	91.5 8.8	87.4 11.0	73.4 8.6	67.4 6.5				
54		93.1 8.7	91.1 7.3	91.1 8.3	80.4 > 10.5	57.8 9.8	Oil 7.3					
55		92.8 9.3	93.2 8.2	93.0 7.6	93.1 7.5	90.6 8.5	71.6 10.0	63.6 7.0	Oil 6.7			
56		92.7 10.1	92.4 9.4	90.0 9.2	87.6 > 10.6	65.9 10.6	61.9 8.7	Oil 8.0				
57		92.5 10.1	92.8 9.6	91.8 8.5	91.5 9.6	89.0 > 9.2	83.0 > 12.2	73.1 10.8	69.2 8.1	67.4 6.6		
58		92.4 9.1	91.2 9.0	89.0 9.1	84.0 > 12.8	71.4 10.5	62.6 7.4					

No.	Cation	Run 1 C_6 [%] Prod.[2]	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
59		92.0 7.9	91.3 7.7	89.5 8.6	86.1 > 9.1	75.2 7.1	66.2 4.5					
60		91.7 9.0	90.3 8.6	90.0 9.0	86.0 9.1	74.0 9.2	66.7 10.0	65.7 6.3	Oil 6.1			
61		91.6 7.6	93.5 8.2	93.3 7.5	93.1 7.6	93.1 8.1	91.8 8.9	91.1 > 11.2	81.8 > 10.5	70.2 8.8	Oil 6.7	
62		91.0 > 11.8	91.7 > 11.4	90.4 > 10.5	89.8 > 12.0	88.0 > 14.0	77.8 > 13.0	74.6 > 12.3	72.0 > 11.3	70.9 > 10.8	66.6 6.8	
63		90.8 > 9.8	91.5 > 10.8	90.3 > 10.0	89.8 > 11.4	88.0 > 11.1	79.8 > 13.7	74.0 9.3	68.3 5.2			
64		90.7 > 10.1	90.0 > 10.0	90.4 > 10.2	90.0 > 10.1	87.7 > 10.5	85.7 > 11.8	72.2 > 10.3	64.4 > 7.4			
65		90.0 > 10.6	89.7 > 9.4	90.0 > 11.5	89.2 > 10.9	89.2 > 12.5	86.2 > 11.6	73.9 > 11.0	68.3 > 9.6	67.5 8.0	64.3 7.0	
66		90.0 > 8.2	90.0 > 9.5	87.5 > 8.7	81.3 > 9.6	71.6 > 9.3	65.3 8.1	65.2 5.8	58.4 4.6			
67		90.0 > 10.9	90.2 > 10.3	89.6 > 10.2	88.1 > 11.2	85.6 > 12.4	76.8 > 10.6	73.7 > 10.6	71.3 8.0	66.5 6.3		
68		90.0 > 8.8	90.6 > 8.6	77.5 > 11.3	60.4 > 8.3							
69		89.9 > 8.4	89.6 > 9.3	90.2 > 9.0	88.8 > 8.2	88.8 > 8.3	88.3 > 10.1	85.1 > 9.1	79.7 > 9.2	67.0 7.3		
70		89.6 > 10.8	90.0 > 10.6	89.7 > 9.4	89.2 > 10.2	88.5 > 11.5	86.0 > 9.2	76.1 > 9.5	70.8 8.0	68.3 5.8		
71		89.6 7.6	86.3 > 8.7	82.6 > 9.7	69.4 > 9.4	Oil > 8.0						

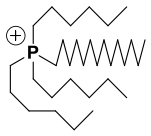
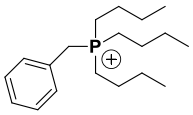
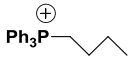
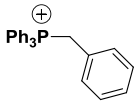
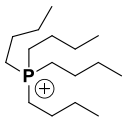
No.	Cation	Run 1 C_6 [%] Prod.[2]	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
72		89.6 > 13.2	73.1 > 13.4	68.2 11.8	66.3 9.2							
73		89.5 > 10.7	89.9 > 12.7	89.0 > 11.6	84.1 > 10.6	75.8 > 11.6	72.7 8.9	67.4 4.5				
74		89.5 > 10.3	89.0 > 11.3	90.0 > 10.6	88.3 > 10.9	80.9 > 12.3	72.0 > 9.3	70.4 8.6	65.6 7.8	60.8 5.8		
75		89.4 > 8.0	89.7 > 8.8	87.3 > 7.9	86.8 > 11.2	84.7 > 9.6	78.8 > 8.9	70.4 > 8.1	68.3 8.6	67.4 8.3	67.5 6.9	
76		89.4 > 10.6	90.0 > 11.1	89.8 > 10.9	88.3 > 10.6	86.3 > 12.7	77.1 > 11.5	70.7 8.6	64.3 4.1			
77		89.1 > 8.7	91.7 > 8.6	91.9 > 8.6	92.5 > 8.6	92.0 > 8.5	90.2 > 8.5	91.6 > 8.3	91.1 > 10.0	89.2 > 10.2	77.4 8.6	73.3 6.1
78		89.0 > 9.4	89.9 > 9.6	88.9 > 11.2	84.8 > 12.1	76.4 > 11.7	74.7 > 11.7	71.7 10.1	66.6 7.3			
79		88.7 > 9.9	88.2 > 9.7	86.7 > 10.9	86.1 > 12.2	80.9 > 12.0	74.6 > 10.5	69.1 7.4	Oil 2.5			
80		88.3 > 8.1	87.0 > 10.1	85.5 > 10.5	81.5 > 10.5	71.1 > 9.7	67.8 7.1	67.2 6.0				
81		88.2 > 10.7	88.6 > 10.6	88.5 > 11.2	87.5 > 11.0	86.5 > 11.9	84.0 > 11.9	79.2 > 13.1	73.4 > 10.2	73.0 > 10.0	73.0 8.8	70.9 7.3
82		88.0 > 8.6	89.7 > 9.5	89.4 > 9.7	88.5 > 10.2	87.8 > 11.5	83.6 > 10.3	76.6 > 10.8	70.5 > 9.2			
83		87.9 > 12.5	88.3 > 12.2	87.5 > 12.3	87.4 > 12.3	83.8 > 12.8	76.0 > 12.9	66.8 8.3				

No.	Cation	Run 1 C_6 [%] Prod.[2]	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
84		87.8 > 9.6	87.1 > 10.5	83.2 > 10.6	Oil > 4.5							
85		87.8 > 10.2	88.7 > 11.4	87.3 > 10.4	87.2 > 10.0	87.2 > 10.7	84.7 > 11.0	79.6 > 12.1	72.9 > 9.9	68.9 7.2	Oil 4.7	
86		84.0 > 10.8	74.4 > 10.9	64.4 > 8.4								
87		78.8 > 9.6	81.9 > 8.6	83.1 > 9.1	81.1 > 8.9	81.9 > 8.9	80.9 > 10.5	76.1 > 9.4	73.2 > 10.0	73.4 > 8.1	73.4 8.1	72.7 6.9
88		75.5 > 11.7	67.5 > 10.2	70.7 > 10.8	69.7 > 9.4	69.6 7.5	73.4 6.9	71.4 5.7	68.0 3.6			
89		73.5 7.6	73.4 8.6	71.6 > 8.9	70.3 > 10.5	70.2 > 10.0	67.1 5.1					
90		63.1 > 9.6	68.4 > 8.2	74.0 6.3	70.3 6.5	73.3 5.7	66.6 4.6					
91		53.7 7.9										
92		Buffered IL solid										

[1] Reaction conditions: 2.5 – 4.0 g buffered ionic liquid; composition $[BiPh_3]$ / $[cation]^+[Al_2Cl_7]^-$ = 0.30; catalyst precursor A; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene; products decanted after each run; > = complete conversion; Oil = only higher oligomers. [2] Productivity given in $g_{product}$ / $g_{ionic\ liquid}$ x h.

Phosphonium Salts

Table 4: Cation screening for nickel catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts (sorted in descending order of selectivities in run 1).[1]

No.	Cation	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
		C_6 [%]						
		Prod.[2]						
93		95.5	90.7	80.3	Oil			
		6.0	9.0	7.7	2.3			
94		92.5	91.1	89.1	79.0	76.1	73.9	Oil
		> 8.6	> 12.0	> 11.5	> 12.5	> 10.6	8.4	4.2
95		91.0	86.5	80.1	71.0	Oil		
		> 11.4	> 11.7	10.4	5.1	3.2		
96		89.4	89.5	89.4	86.9	75.7	75.1	68.8
		> 8.8	> 10.0	> 11.2	> 12.8	> 12.6	8.3	4.5
97		85.4	73.0	64.0	67.4	Oil		
		> 18.7	> 18.5	14.1	11.3	6.9		
98		78.1	77.8	70.4	65.9			
		> 10.1	> 11.7	> 10.1	> 7.9			
99		68.6	63.1	63.0	63.6	63.7	63.4	
		> 11.1	> 12.0	> 11.8	> 15.3	> 10.7	5.9	
100		49.5	60.2	55.3	Oil			
		> 11.2	> 11.2	6.9	6.3			

[1] Reaction conditions: 2.5 – 4.0 g buffered ionic liquid; composition $[BiPh_3]$ / $[cation]^+[Al_2Cl_7]^-$ = 0.30; catalyst precursor A; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; stirring rate = 1200 min^{-1}; t = 60 min; 300 ml glass autoclave; 40 – 60 ml liquid propene; products decanted after each run; > = complete conversion; Oil = only higher oligomers. [2] Productivity given in $g_{product}$ / $g_{ionic\ liquid}$ x h.

6.4.4 References

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7 Buffered Aluminum Chloride as Highly Efficient Cocatalyst for Olefin Dimerization and Polymerization Reactions

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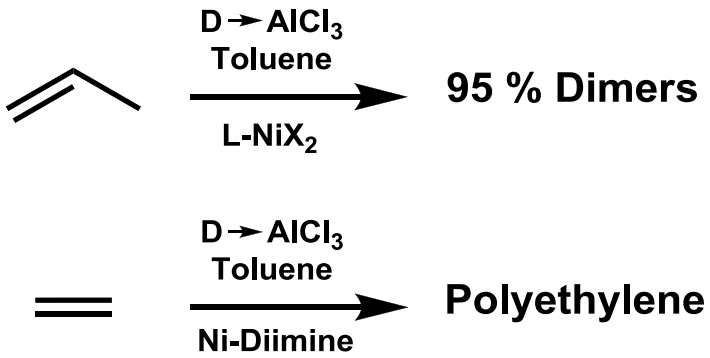
Keywords: cocatalysts, nickel, dimerization, polymerization, ionic liquids

Manuscript to be submitted



Abstract: We developed a binary cocatalyst system based on simple aluminum chloride and weak Lewis bases like triphenylbismuth or N-methylpyrrole. A donor-acceptor interaction kept the aluminum chloride dissolved in toluene or methylene chloride. The systems were investigated by ^{27}Al NMR spectroscopy and were successfully applied as cocatalysts in nickel catalyzed dimerization and polymerization reactions of α-olefins. Their Lewis acidities correlated to the line width of the ^{27}Al NMR signals and were influenced by the solvent and the type and amount of buffer. For

propene dimerization reactions, dimer selectivities of up to 95% were achieved. Ethene was dimerized to give butenes (up to 92%), of which 79% were 1-butene. With a Brookhart type nickel diimine complex, ethene was polymerized with a cocatalyst solely based on aluminum chloride. Up to 38 wt% of the reaction products were polyethylene with a typical molecular weight of 140 kg/mol. The donor-acceptor interactions of triphenylbismuth and N-methylpyrrole with aluminum chloride were successfully transferred to Lewis acidic chloroaluminate ionic liquids. Ethene was polymerized with a nickel diimine complex dissolved in buffered chloroaluminate ionic liquids in the absence of alkylaluminum groups for the first time.

7.1 Introduction

Since Ziegler described the “nickel effect” being responsible for the catalytic formation of butenes from ethene in 1955[1], a lot of research has been done on nickel catalyzed selective olefin dimerization and oligomerization reactions.[2] Two major industrial processes were established using metal organic nickel catalysts.

The Shell higher olefin process (SHOP) uses a nickel complex with a [P,O] chelate ligand,[3] which catalyzes ethene oligomerization reactions to give α-olefins (**Figure 1**). With the latest unit in Geismar (USA), Shell increased its total ethene oligomerization capacity to 1.5 million tons per year in 2002.[4] This equals more than half of the total amount of ethene oligomers produced worldwide.[4] The catalyst is dissolved in 1,4-butanediol, which is immiscible with the oligomers produced from ethene. Thus, product separation can be achieved simply by decantation.[5] Although the selectivity to both linearity and terminal olefin functionality is almost quantitative, oligomers are obtained in a Schulz-Flory-type distribution.[6] Therefore, a SHOP plant also consists of a distillation unit to extract the valuable product fractions, while higher oligomers are isomerized and subjected to a metathesis step with ethene in order to maximize the yield of valuable products.[3b] In contrast to many other nickel based dimerization or oligomerization systems, SHOP catalysts are active without additional activators. Hence, the process is operated under more drastic conditions compared to nickel systems activated with aluminum based cocatalysts. Typically, these reactions are performed at 80 – 140°C with pressures between 7 and 14 MPa.[6]

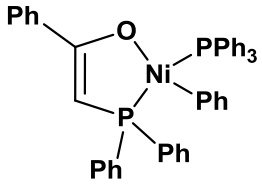


Figure 1: Structure of a typical catalyst used in the Shell higher olefin process.[7]

The DIMERSOL® technology is the second large industrial process catalyzed by nickel complexes. It was developed by Chauvin *et al.* in the 1970s[8] and is used commercially by the Institut Français du Pétrole (IFP) to dimerize propene (DIMERSOL® G) or 1-butene (DIMERSOL® X) selectively. The catalytic system uses the principles of the "nickel effect" described by Ziegler.[1a] Nickel(II) salts or complexes are activated in situ by alkylaluminum compounds, mostly ethylaluminum dichloride. The Lewis acidic aluminum cocatalyst transfers an alkyl group to the nickel center and generates catalytically active cationic nickel hydrido or alkyl complexes (**Figure 2**).[2a, 9] Monomers are inserted into the Ni–C or Ni–H bonds and eliminated by β-H elimination. No solvents are necessary, the homogeneous reactions are operated at mild conditions of 1.5 MPa and 40 – 60°C directly in the olefin feeds.[6] Currently, 35 licensed DIMERSOL® units with typical capacities between 20000 and 90000 tons per year are in use for selective dimerization reactions of short chain olefins.[9a, 9c]

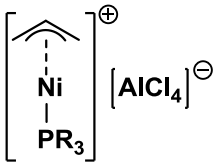
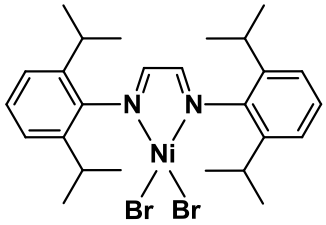


Figure 2: Nickel catalyst for propene dimerization reactions in the DIMERSOL® process.[10]

While the SHOP process produces a wide distribution of oligomers from ethene, DIMERSOL® units selectively dimerize 1-butene to give around 80% octenes.[9c] However, the use of alkylaluminum cocatalysts makes the DIMERSOL® system very sensitive versus oxygen or polar impurities. Furthermore, neither the catalysts nor the cocatalysts can be recycled in this homogeneous reaction.[11]

Nickel complexes are not only used for olefin oligomerization and dimerization reactions, they were also found to be efficient for olefin polymerization reactions. In 1995, Brookhart *et al.* first described ethene polymerization reactions with highly active nickel complexes based on novel bulky diimine ligands activated with methylaluminoxane (MAO).[12] Before, polymerization only occurred occasionally with such Ziegler type nickel oligomerization systems. However, predictions how catalysts and ligands have to be designed to produce polymers selectively were difficult.[3b] In the last ten years, SHOP type catalysts were optimized to polymerize ethene, too.[7, 13] However, their activity cannot compete with MAO activated nickel diimine systems. Due to the intensive research launched by a Brookhart report, many nickel diimine based olefin polymerization catalysts are known today.[14]

While the SHOP catalyst consists of a single component, which usually displays low activity, most of the nickel based dimerization or polymerization systems rely on aluminum based activators. Common cocatalysts are MAO and its derivatives, ethylaluminum dichloride, diethylaluminum chloride, triethylaluminum, trimethylaluminum, or mixtures thereof.[1a, 12, 14-15] Unfortunately, all aluminum cocatalysts used so far bear an alkyl group in order to guarantee their solubility in nonpolar organic solvents as well as to reduce their Lewis acidity compared to aluminum trichloride.[16] The latter catalyzes side reactions like isomerization, cracking, disproportionation of alkanes as well as alkylation of aromatics with alkenes and cationic oligomerization of olefins.[17] Furthermore, the proposed mechanism based on the insertion of monomers into Ni–H or Ni–C bonds of nickel(II) complexes requires an alkylating agent. Alkylaluminum compounds are pyrophoric and highly sensitive to water, oxygen, or polar impurities. Thus, they are mostly the cost determining factor for commercial applications. Feed streams have to be purified thoroughly prior to the reactions, and the high reactivity requires a cautious handling. Finally, the cocatalysts are destroyed upon product separation of the homogeneous reactions.[8c] Also, alkylaluminum cocatalysts contribute to the deactivation of active Ni(II) catalysts by reducing Ni(II) to its zero oxidation state.[18] Therefore, the development of insensitive $AlCl_3$ based cocatalyst systems would be highly desirable in terms of process economics.



1

Figure 3: Brookhart type nickel diimine complex used for ethene polymerization reactions with buffered $AlCl_3$ activators.

Ionic liquids synthesized from $AlCl_3$ are an elegant attempt to overcome the recycling and solubility restrictions of systems based solely on $AlCl_3$.[19] In combination with certain organic cations, $AlCl_3$ forms liquids at ambient temperature over a wide range of compositions, which are immiscible with hydrocarbon phases. The Lewis acidities of such chloroaluminate ionic liquids can be adjusted from basic over neutral to acidic simply by varying the $AlCl_3$ / halide salt ratio.[20] However, basic or neutral liquids do not activate nickel catalysts, while acidic compositions predominantly catalyze side reactions like uncontrolled cationic oligomerization of olefins[17b, 21] as well as isomerization[22] and cracking[23] reactions of saturated alkanes.

Chauvin *et al.* suppressed such cationic olefin oligomerization reactions by the addition of $EtAlCl_2$ to slightly acidic chloroaluminate melts. These melts were able to activate nickel complexes for selective dimerization reactions of α-olefins.[24] The IFP brought this so called DIFASOL® process to industrial application by retrofitting it to their existing homogeneous DIMERSOL® units.[9c, 10-11] However, the use of ethylaluminum dichloride restricts the use of DIFASOL® systems. They can only be operated in combination with DIMERSOL® units, which previously remove all impurities from the feed stream. Otherwise, impurities would accumulate in the ionic liquid, and recycling of the melt after its depletion is not intended.[9a, 9c]

In 1998, Wasserscheid reported the first biphasic system for nickel catalyzed olefin dimerization reactions exclusively based on $AlCl_3$.[25] He used weak organic bases like pyridine, quinoline, or pyrrole derivatives to reduce the "latent acidity"[26] of chloroaluminate ionic liquids. The interaction of the nitrogen bases with $AlCl_3$ or the $[Al_2Cl_7]^-$ species present in such liquids[19a, 27] suppressed uncontrolled cationic olefin

oligomerization reactions. The buffered chloroaluminate melts were used to activate nickel complexes for selective dimerization reactions of various α-olefins.[28]

Single component equivalents of the Lewis base interaction with aluminum in ionic liquids are intramolecular donor-stabilized aluminum cocatalysts. Several of such aluminum compounds stabilized by pending intramolecular nitrogen,[29] phosphorus,[30] oxygen,[31] or sulfur[32] groups have been described and used as cocatalysts. However, these intramolecular stabilized aluminum compounds often require large synthetic efforts and still contain reactive Al–C bonds. Therefore, they are no cheap alternative to common alkylaluminum cocatalysts for large commercial applications.

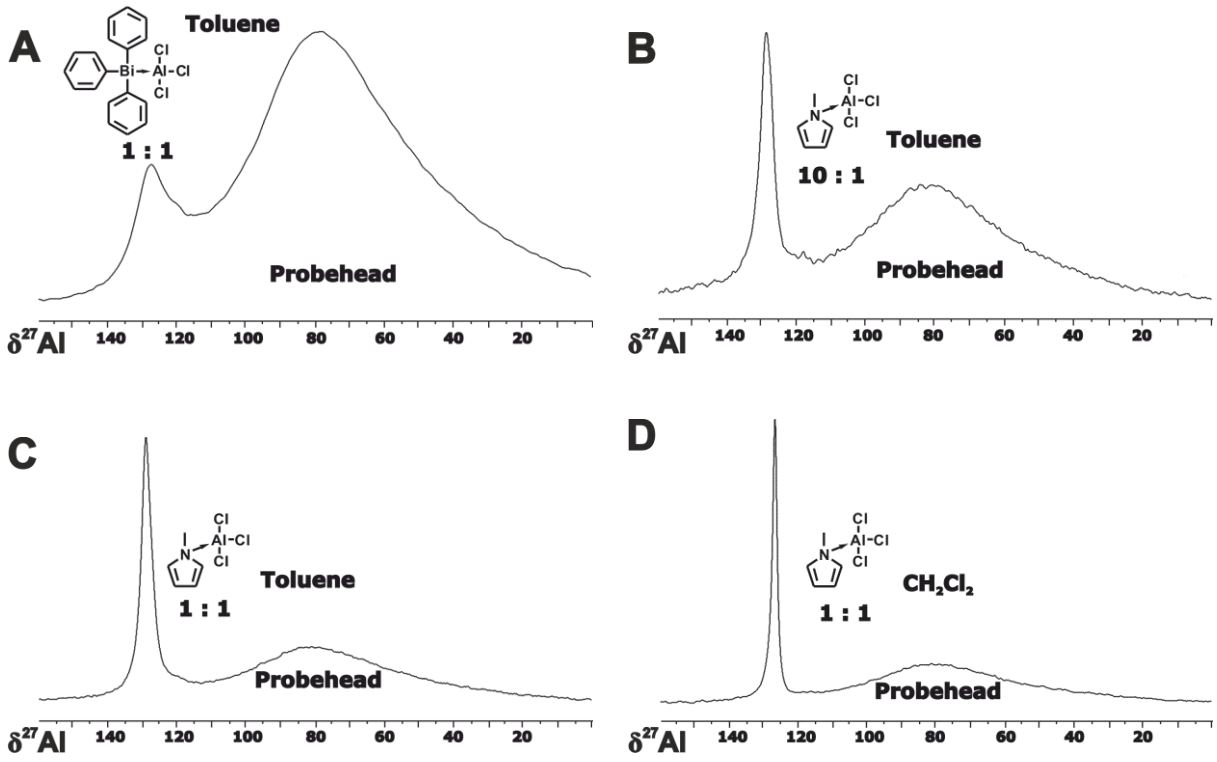
Recently, we described the use of triphenylphosphine and triphenylbismuth as highly efficient buffers for Lewis acidic chloroaluminate ionic liquids[33] and investigated the interaction of the basic phosphine center with the Lewis acidic aluminum species by ^{27}Al NMR and ^{31}P NMR spectroscopy.[34] In the course of our search for cheap and insensitive cocatalysts for nickel catalyzed olefin dimerization and polymerization reactions, we extended the concept of buffering highly Lewis acidic aluminum chloride centers to two component homogeneous systems.

7.2 Results and Discussion

NMR Investigations of Donor-Acceptor Interactions of Aluminum Chloride with N-Methylpyrrole and Triphenylbismuth

The most efficient buffers for Lewis acidic chloroaluminate melts were found to be N-methylpyrrole[28a] (N-MP) and triphenylbismuth.[33] Therefore, we first investigated what happened to $AlCl_3$ in toluene if equimolar amounts of these two buffers were added. Surprisingly, the initially insoluble anhydrous $AlCl_3$ completely dissolved upon buffer addition. Obviously, the donor-acceptor interaction between the buffer and the Al center was sufficient to break up the dimeric Al_2Cl_6 structure of aluminum chloride. The organic buffer strongly increased the solubility of $AlCl_3$ by forming a weak adduct. It was also possible to dissolve buffer adducts of aluminum chloride in CH_2Cl_2. However, in the case of N-MP, the system started to flocculate slowly. We assume that the strong Lewis acid $AlCl_3$ catalyzed a ring opening reaction of the nitrogen heterocycle. No precipitation

occurred with the triphenylbismuth adduct over several hours. We examined these interactions by ^{27}Al NMR spectroscopy (**Scheme 1**).



Scheme 1: ^{27}Al NMR spectra of the donor-acceptor interaction of $AlCl_3$ with different donors at 25°C (**A**: 1 equivalent $BiPh_3$, 0.05 N $AlCl_3$ in toluene, trace C_6D_6; **B**: 10 equivalents N-MP, 0.1 N $AlCl_3$ in toluene, trace C_6D_6; **C**: 1 equivalent N-MP, 0.1 N $AlCl_3$ in toluene, trace C_6D_6; **D**: 1 equivalent N-MP, 0.1 N $AlCl_3$ in CH_2Cl_2, trace $CDCl_3$;).

The measurements were performed in toluene with a few drops of C_6D_6 and in CH_2Cl_2 with additional $CDCl_3$. The aluminum containing probehead of the NMR spectrometer appeared around δ = 80 ppm as broad signal. For $BiPh_3$ adducts, an $AlCl_3$ concentration of 0.05 N was chosen. The solubilities of N-MP adducts were higher, and thus, a 0.1 N system was measured. The compounds were mixed and the spectra recorded within a few minutes due to the decomposition of $AlCl_3$ / N-MP adducts. All ^{27}Al NMR signals appeared around δ = 128 ppm. However, the broadness of the signals differed strongly. The broadest peak was observed for the $BiPh_3$ / $AlCl_3$ interaction in toluene with a line width at half maximum of 1200 Hz (A). With a ten fold excess of N-MP in toluene, the line width was 480 Hz (B) while it decreased to 330 Hz with only one equivalent of N-MP (C). The sharpest signal with a line width at half maximum of 190 Hz

was obtained from an equimolar composition of $AlCl_3$ and N-MP in methylene chloride (D). The shoulders in spectra A and B probably belong to decomposition products, which were not identified. The shoulder increased for system B over time.

The broadness of the ^{27}Al NMR signal allowed conclusions about the extent of the donor-acceptor interaction. For example, the ^{27}Al NMR signal was broadened if ten equivalents instead of one equivalent of N-MP were added. In contrast, the interaction between N-MP and $AlCl_3$ in methylene chloride was less intensive indicated by a relatively sharp signal. The more polar solvent methylene chloride interacted more strongly with the adduct increasing the average distance between the donor and the acceptor.

Homogeneous Propene Dimerization Reactions

Further, we were interested if such adducts still displayed sufficiently high Lewis acidities to activate nickel complexes. In buffered ionic liquids, only small amounts of buffer compared to the $AlCl_3$ content were employed. For $AlCl_3$ / buffer adducts in homogeneous solution at least equimolar amounts of buffer were necessary to dissolve aluminum chloride.

In a first series of experiments we tried to activate $(PCy_3)_2NiCl_2$ with 850 equivalents of the homogeneous $AlCl_3$ adducts in order to selectively dimerize propene. Sterically demanding phosphine ligands like tricyclohexylphosphine were known to favour the formation of valuable highly branched dimers in nickel catalyzed dimerization reactions.[2a, 15e, 16] The formation of 2,3-dimethylbutenes is highly desirable due to their high research octane number (RON). They can be sold as high octane motor fuels or used to increase the RON of low octane fractions.[35]

All experiments successfully produced dimers (**Table 1**). The triphenylbismuth adduct yielded 72% dimers in toluene (1) and 59% dimers in CH_2Cl_2 (2). Even when the CH_2Cl_2 solvent was removed after adduct formation, the solvent free system yielded 73% dimers (3). Thus, the adduct was soluble in olefins like propene, too. The best result was obtained with N-MP in toluene with 95% C_6 products (4). All $AlCl_3$ compositions displayed enormous activities up to almost 32 ton per mol nickel and hour (2). For systems with higher selectivities to C_6, the activities decreased while higher activities were obtained with less selective systems. The highest content of 2,3-dimethylbutenes

was produced with $BiPh_3$ in toluene (53%). Generally, reactions in toluene were more selective than reactions in CH_2Cl_2. This was in accordance with our ^{27}Al NMR investigations. A sharper ^{27}Al NMR signal indicated a weaker donor-acceptor interaction, and thus, a higher Lewis acidity compared to toluene based systems. The results indicated that the N-MP buffer was superior to triphenylbismuth in terms of dimer selectivity. In contrast, $BiPh_3$ reduced the rates of ligand abstraction more efficiently. Triphenylbismuth buffered systems always yielded higher 2,3-dimethylbutene contents than similar N-MP buffered compositions. This might also be attributed to additional π-interactions of the three aromatic rings in $BiPh_3$. The addition of aromatic additives was found to maintain the phosphine effect over extended periods of time.[24b] Certainly, systems buffered by a combination of N-MP and $BiPh_3$ should result in high selectivities to both dimers and 2,3-dimethylbutenes.

For comparison, three experiments using an ethylaluminum dichloride cocatalyst in toluene were also performed. Without buffer, only 36% dimers were formed under the applied reaction conditions (5). If equimolar amounts of $BiPh_3$ or N-MP were added to the ethylaluminum dichloride solution, the dimer selectivities drastically increased to 75% (6) and 95% (7), respectively. As can be seen from both $AlCl_3$ and $EtAlCl_2$ based systems, higher dimer selectivities came along with higher degrees of branching and reduced activities. Thus, such systems provide a lot of possibilities to optimize the results simply by varying parameters like solvents, buffer excess or type and amount of ligand.

Definitely, buffered aluminum based cocatalysts are a promising alternative to alkylaluminum systems used in DIMERSOL® plants. Especially the insensitive N-MP / $AlCl_3$ adducts can easily replace $EtAlCl_2$ or Et_2AlCl cocatalysts. Upon hydrolysis, residual N-MP can remain in the product phase if it is used to blend gasoline, while only very cheap aluminum chloride is consumed. Aluminum chloride as well as triphenylbismuth and N-MP can be stored in air and unlike aluminum alkyls, they do not require an extremely cautious handling. The components can be mixed quickly prior to use. Thus, the very slow decomposition of N-MP is negligible under the applied conditions.

Table 1: Homogeneous nickel catalyzed propene dimerization reactions with buffered $AlCl_3$ cocatalysts.[1]

No.	Lewis Acid	Buffer	Solvent	C_6 [%]	HEX [%]	MP [%]	DMB [%]	Activity[2]
1	$AlCl_3$	$BiPh_3$	Toluene	71.6	7	40	53	10.24
2	$AlCl_3$	$BiPh_3$	CH_2Cl_2	59.1	22	73	5	31.72[3]
3	$AlCl_3$	$BiPh_3$	–	73.0	19	57	24	2.67
4	$AlCl_3$	N-MP	Toluene	95.3	17	59	24	5.55
5	$EtAlCl_2$	–	Toluene	36.1	22	72	6	8.76
6	$EtAlCl_2$	$BiPh_3$	Toluene	75.2	4	41	55	7.62
7	$EtAlCl_2$	N-MP	Toluene	95.3	11	53	36	1.13

[1] Reaction conditions: 3 – 6 mg $(PCy_3)_2NiCl_2$; [Al] / [Ni] = 850; [Al] / [buffer] = 1; 50 ml solvent; T = 40°C; stirring rate = 600 min^{-1}; t = 60 min; stirred 300 ml Parr stainless steel autoclave; 200 ml liquid propene; HEX = *n*-hexenes; MP = 2-methylpentenes; DMB = 2,3-dimethylbutenes; N-MP = N-methylpyrrole. [2] $t_{product}$ / mol_{Ni} x h. [3] Extrapolated; reaction was stopped after 30 min due to an extremely high activity.

Homogeneous Ethene Polymerization Reactions

Since nickel complexes were successfully activated to dimerize propene with our system, we extended the study for ethene polymerization reactions. Therefore, a typical Brookhart type nickel diimine complex was employed as catalyst precursor (**Scheme 2**). The complex is known to polymerize ethene upon activation with methylaluminoxane or Et_2AlCl.[12, 14b, 14c]

Table 2 summarizes the results of the ethene polymerization reactions with complex **1**. In all experiments employing triphenylbismuth or N-methylpyrrole as buffer, polymers were produced (**Table 3**). While the toluene based catalysts 8 – 10 yielded polyethylenes with similar molecular weights around 140 kg/mol, the system dissolved in methylene chloride yielded polyethylene with a molecular weight of only 75 kg/mol (11). Certainly, this effect was attributed to the increased Lewis acidity in methylene chloride. Among all toluene based systems, the triphenylbismuth buffered system (8)

led to the polyethylene with the highest PDI in combination with the lowest degree of crystallinity and the lowest melting point. Remarkably, the PDI of the polyethylene obtained with the N-methylpyrrole buffered system was reduced from 2.55 (9) to 2.25 (10) by the addition of an excess of five equivalents of buffer while molecular weights, melting points, and degrees of crystallinity remained unchanged.

Table 2: Homogeneous nickel catalyzed ethene polymerization reactions with buffered $AlCl_3$ cocatalysts.[1]

No.	Solvent	Reaction Time [min]	Buffer	[Al] / [Ni]	PE [wt%]	Oligomers [wt%]	C_4 [%][2]	1-C_4 [%][3]	Activity[4]
8	Toluene	30	$BiPh_3$	500	38	62	83.3	67.6	1.48
9	Toluene	30	N-MP	500	7	93	87.0	53.7	2.77
10	Toluene	30	N-MP	500[5]	19	81	91.5	79.4	0.69
11	CH_2Cl_2	10	$BiPh_3$	200	12	88	71.9	20.2	16.54
12	CH_2Cl_2	60	PPh_3	500	0	100	not det.	not det.	0.04

[1] Reaction conditions: 8 – 15 mg catalyst precursor 1; $AlCl_3$ activator; [buffer] / [Al] = 1; 50 ml solvent; T = 40°C; stirring rate = 600 min^{-1}; stirred 300 ml Parr stainless steel autoclave; 10 bar ethene; PE = polyethylene; N-MP = N-methylpyrrole. [2] Molar amount of butenes within oligomer fraction. [3] Molar amount of 1-butene within butenes. [4] $t_{product}$ / mol_{Ni} x h. [5] [buffer] / [Al] = 5.

However, large amounts of oligomers were formed besides the polyethylenes. The highest polymer content of 38 wt% was obtained with $BiPh_3$ in toluene at an Al to Ni ratio of 500 (8). After the buffer was used in excess to aluminum chloride, the polymer content could be increased from 7 wt% for the equimolar composition (9) to 19 wt% with a five fold excess of N-MP in toluene (10).

Table 3: Polyethylene properties.

No.	M_n [kg/mol]	M_w [kg/mol]	PDI	T_m [°C]	X_c [%][1]
8	49	141	2.87	114.6	4
9	55	141	2.55	121.1	32
10	60	134	2.25	121.8	30
11	26	75	2.88	105.4	2

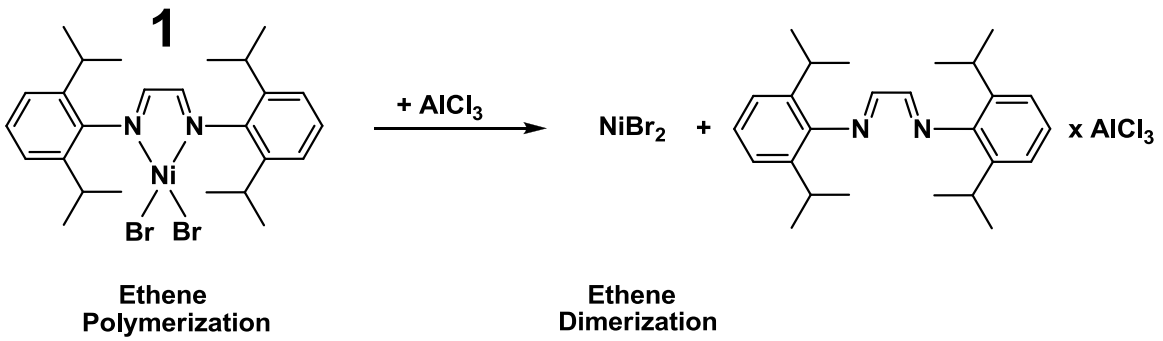
[1] Crystallinity calculated with ΔH_m = 293 J/g for 100% crystalline PE.

To summarize, the triphenylbismuth buffer led to the formation of higher amounts of polymers compared to N-methylpyrrole. In contrast, N-methylpyrrole buffered systems yielded polyethylenes with higher degrees of crystallinity and smaller PDIs. Thus, these buffered aluminum chloride based cocatalyst systems provide a lot of possibilities to maximize the yield of polymers and to influence their properties.

Surprisingly, the oligomers formed as by-products consisted mainly of dimers. The system with excess N-MP produced 81 wt% oligomers (10), of which 92% were butenes. Even the selectivity to give 1-butene among these butenes was outstanding with 79%. Obviously, higher buffering levels came along with lower isomerization rates and, thus, large amounts of α-olefinic dimers were formed. Triphenylphosphine, which was able to buffer Lewis acidic chloroaluminate melts,[34] was also tested in addition to $BiPh_3$ and N-MP for its ability to activate the nickel complex in combination with $AlCl_3$. Although $AlCl_3$ dissolved in CH_2Cl_2 upon contact with PPh_3, the resulting solution was almost inactive and produced no polymer (12).

An explanation for the formation of polymers competing with highly selective olefin dimerization reactions is given in **Scheme 2**. The diimine ligand with its bulky isopropyl substituents is mandatory for the nickel center to polymerize ethene. However, the Lewis acidic aluminum chloride center competes with the nickel center for the Lewis basic diimine ligand. As soon as the ligand is abstracted from the metal center, the nickel complex is no longer able to polymerize ethene. Instead, the remaining nickel bromide is a very efficient dimerization catalyst upon activation.[36] The same behaviour

was observed for the content of highly branched 2,3-dimethylbutenes in the case of propene dimerization reactions. As soon as the sterically demanding tricyclohexylphosphine ligands are abstracted from the nickel center, the formation of 2,3-dimethylbutenes is stopped.



Scheme 2: Abstraction of the diimine ligand of complex **1** by $AlCl_3$.

The results of the ethene polymerization reactions also confirmed our theory that $BiPh_3$ suppressed the ligand abstraction more efficiently than N-MP. In triphenylbismuth based systems (8, 11), the polymer yields were higher than in N-MP buffered systems (9, 10). However, after ligand abstraction, the N-MP buffered systems displayed higher selectivities to give butenes. Also, the isomerization of 1-butene to yield 2-butenes was reduced in less acidic systems and with higher buffer contents. These results suggested that such nickel based ethene dimerization systems are capable of producing α-olefins with high selectivities. However, subsequent isomerization reactions disguised the real product distributions.

The catalytic results indicated that the mechanism of these homogeneous aluminum chloride based systems was similar to the mechanism we proposed for nickel catalyzed olefin dimerization reactions in buffered chloroaluminate ionic liquids.[33] Upon contact with aluminum chloride, a nickel halide complex forms $Ni(AlX_4)_2$ (X = Cl, Br) species[37] with weakly coordinating tetrahaloaluminate anions. While strongly coordinating ligands, e.g. bidentate diimines or monodentate basic phosphines, remain at the active nickel center, the weakly coordinating $[AlX_4]^-$ anions can easily be replaced by olefins or buffer molecules. Since no alkylating agent was present in these systems, we also assume that the catalytic cycle started with the formation of nickelacyclopentane.[33]

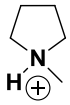
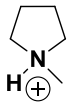
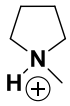
Biphasic Ethene Polymerization Reactions in Buffered Chloroaluminate Ionic Liquids

Not many ionic liquid based systems have been described in the literature so far which were able to polymerize α-olefins. In 1990, titanocene dichloride was found to produce polyethylene when dissolved in alkylchloroaluminate ionic liquids.[38] However, the system displayed a poor activity and failed to activate other metallocene complexes. Ethene polymerization reactions catalyzed by nickel diimine complexes in neutral chloroaluminate ionic liquids have also been reported twice. However, the systems were only active if MAO was added to the ionic liquid,[39] and subsequently, they did not provide a serious alternative to homogeneous MAO activated systems in terms of process economics.

After we successfully polymerized ethene with a nickel diimine complex and buffer adducts of $AlCl_3$ in homogeneous solution, the same catalyst precursor was employed for biphasic ethene polymerization reactions in buffered chloroaluminate ionic liquids (**Table 4**). Unexpectedly, all systems produced polyethylenes. With 0.60 equivalents of $BiPh_3$ buffer in a maximum acidic N-methylpyrrolidine hydrochloride based ionic liquid, 20 wt% of the product fraction consisted of polymer (13). The same composition with N-MP buffer only yielded 1 wt% polymer and 99 wt% dimers and oligomers (15). Since no reactive alkylaluminum groups were present in such buffered chloroaluminate melts, simple amine hydrochlorides could be used instead of quaternary ammonium salts. This is a big advantage since depleted systems can be recycled simply by acid base extraction.[33]

Even a standard $EtAlCl_2$ buffered DIFASOL® composition produced 4 wt% polyethylene (16). In order to improve the polymer yield, the DIFASOL® composition was further buffered with 0.06 equivalents of $BiPh_3$. The additional buffer increased the polyethylene production to 12 wt% (17). Similar to previous homogeneous propene dimerization and ethene polymerization reactions, triphenylbismuth was more efficient than N-MP in suppressing the abstraction of the diimine ligand from the nickel center in these biphasic systems.

Table 4: Nickel catalyzed biphasic ethene polymerization reactions in buffered chloroaluminate melts.[1]

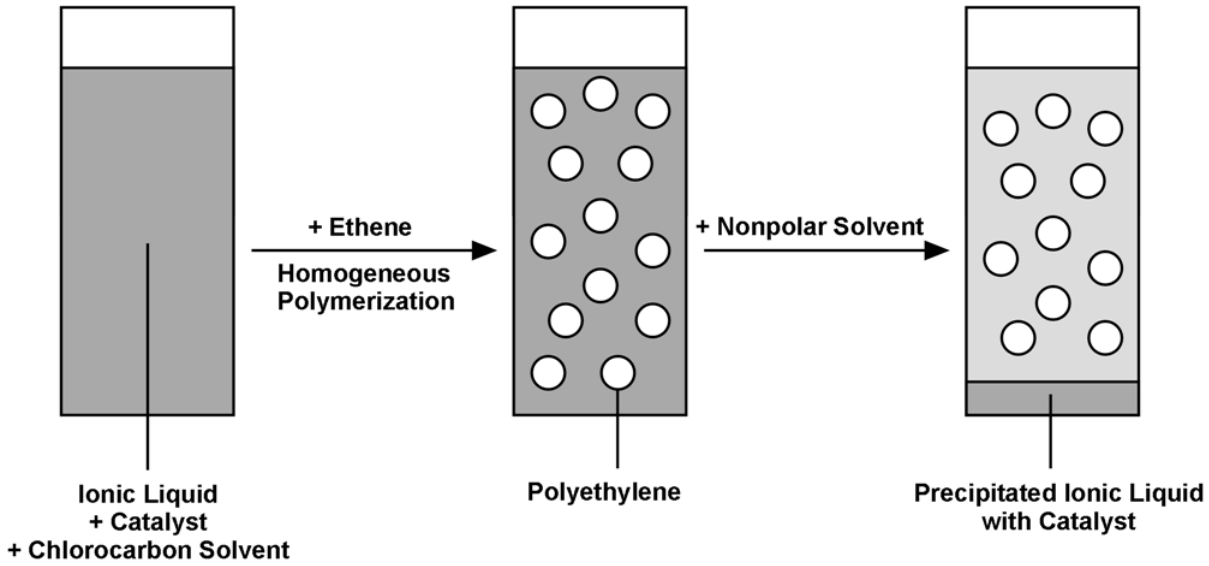
No.	Cation	$[AlCl_3]$ / [Cation]	Buffer	[Buffer] / [Cation]	PE [wt%]	M_w[2]	PDI	X_c [%][3]	T_m [°C]	Prod.[4]
13		2.00	$BiPh_3$	0.60	20	147	2.76	28	121.9	23.4
14		2.00[5]	$BiPh_3$	0.60	10	46	2.51	3	109.9	59.7
15		2.00	N-MP	0.60	1	143	2.65	18	120.4	65.8
16		1.20	$EtAlCl_2$	0.20	4	146	2.85	4	110.4	180.6[6]
17		1.20	$EtAlCl_2$ $BiPh_3$	0.20 0.06	12	196	2.86	23	117.8	34.1

[1] Reaction conditions: 3.9 – 4.5 g buffered ionic liquid; catalyst precursor 1; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 40°C; stirring rate = 600 min^{-1}; t = 30 min; stirred 300 ml Parr stainless steel autoclave; 10 bar ethene and 50 ml *n*-heptane solvent for ethene experiments. PE = polyethylene; N-MP = N-methylpyrrole. [2] kg/mol. [3] Crystallinity calculated with ΔH_m = 293 J/g for 100% crystalline PE. [4] Productivities given in $g_{product}$ / $g_{ionic\ liquid}$ x h. [5] Ionic liquid dissolved in 150 ml CH_2Cl_2. [6] Calculated; reactor capacity reached after 10 min.

In contrast to homogeneous systems, the degree of crystallinity was higher for the triphenylbismuth system (13) compared to the N-MP buffered system (15), while molecular weights, PDIs, and melting points were comparable. The polyethylene produced with 16, which was only buffered by $EtAlCl_2$, displayed almost no crystallinity. With additional triphenylbismuth (17), the polyethylene was more crystalline, and its molecular weight increased to 196 kg/mol, while the PDI remained constant.

Biphasic nickel catalyzed olefin conversion reactions are limited by mass transport of the olefins and not by the catalyst above a certain catalyst concentration.[28c] Thus, the productivities, which are related to the total amount of ionic liquid, were given instead of

activities.[33] Since ethene polymerization reactions occurred at the surface of the ionic liquids, mixing became a problem with increasing polymer contents. Therefore, the ionic liquid was dissolved in CH_2Cl_2 leading to a homogeneous system. After the reaction, the ionic liquid was not soluble within the solvent / product mixture anymore due to a lower polarity resulting from the oligomeric side products, and it precipitated at the bottom. In this case, 10 wt% of polymer were formed (14). Like in the homogeneous reactions, the presence of methylene chloride reduced the molecular weight to 46 kg/mol (14) compared to 147 kg/mol found for the polyethylene from the solvent free system (13). However, solvent dilution of such ionic liquid polymerization systems could be a promising attempt to use the advantages of homogeneous catalysis combined with the ease of separation of a biphasic system (**Scheme 3**).



Scheme 3: Homogeneous ionic liquid based ethene polymerization reactions and subsequent catalyst recovery by precipitation.

Precipitation can either be initiated by the addition of any nonpolar hydrocarbon solvent, or it occurs automatically due to the dimerization products formed. Ideally, such a system would be able to synthesize both valuable polyethylene and α-olefinic oligomers in just one step. For example, the formation of 1-butene in combination with ethene polymerization catalysts could lead to LLDPE copolymers from ethene in a one pot reaction.

Conclusion

We developed a new class of cocatalysts for nickel catalyzed olefin dimerization and polymerization reactions. In combination with weak Lewis bases such as $BiPh_3$ or N-methylpyrrole, $AlCl_3$ readily dissolves in olefinic, aromatic, or chlorocarbon solvents. The Lewis acidities of such donor-acceptor solutions could be tuned precisely to mimic the properties of common cocatalysts like $EtAlCl_2$ or Et_2AlCl. Since no highly reactive and pyrophoric alkylaluminum groups are present, the $AlCl_3$ adducts are much cheaper, easier to handle and less sensitive to impurities. ^{27}Al NMR spectroscopy was used to investigate the buffer / $AlCl_3$ interactions in toluene and methylene chloride. Strong interactions resulted in broad signals and weak Lewis acidic compositions. In contrast, cocatalyst systems with sharp ^{27}Al NMR signals displayed high Lewis acidities. The $AlCl_3$ based cocatalyst was successfully employed to activate nickel catalysts for selective dimerization and polymerization reactions of α-olefins. Propene dimerization reactions yielded up to 95% dimers. For ethene, a maximum selectivity of 92% butenes was achieved. Remarkably, 79% of these were the valuable 1-butene. With bulky diimine ligands attached to the nickel center, the system could switch from ethene dimerization to ethene polymerization reactions. By varying the solvent and the type and amount of buffer, the polymer yield was increased to give up to 38 wt% polyethylene. The molecular weights were found to be around 140 kg/mol with PDIs between 2 and 3.

Furthermore, ethene was polymerized with a nickel diimine complex dissolved in chloroaluminate ionic liquids in the absence of alkylaluminum groups for the first time.

Triphenylbismuth and N-MP are able to buffer aluminum chloride as well as $EtAlCl_2$. Thus, the combination of different buffers, solvents, and aluminum compounds allows the preparation of tailor made cocatalysts for nickel catalyzed olefin dimerization and polymerization reactions.

7.3 Experimental Section

General Information

All chemical manipulations were carried out using standard Schlenk techniques under argon atmosphere. *n*-Heptane and *n*-pentane were distilled from Na/K alloy under inert

atmosphere. Methylene chloride was distilled in two steps from P_4O_{10} and CaH_2, toluene from P_4O_{10} and Na/K alloy. NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. ^{27}Al NMR chemical shifts are given to ± 0.4 ppm relative to external 1.1 M $Al(NO_3)_3$ in D_2O [δ ^{27}Al = 0 ppm for Ξ (^{27}Al) = 26.056890 MHz]. The products of the dimerization experiments were characterized by gas chromatography (Agilent 6850) and GC-MS (FOCUS DSQ™ Thermo Scientific). Differential scanning calorimetry experiments were conducted at a heating rate of 10°C/min under N_2 atmosphere with a Perkin-Elmer Diamond DSC, calibrated with indium. The endothermic maximum of the second heating cycle was taken as T_m. The molecular weights (M_w/M_n) of the ethylene polymers were determined by gel permeation chromatography on a Polymer Laboratories Ltd. (PL-GPC220) chromatograph at 150°C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% weight/volume) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polystyrene (M_w = 510 – 3100000 g/mol) standards using the universal calibration method.[40] The reported values are the average of at least two independent determinations.

Ethene (99.9%) and propene (99.3%) were purchased from Riessner Gase, Lichtenfels, and were dried over a column packed with P_4O_{10}. $EtAlCl_2$ (0.9 M in heptane) and 1-ethyl-3-methylimidazolium chloride were purchased from Acros and used without further purification. Triphenylphosphine and triphenylbismuth were purchased from ABCR. $(PCy_3)_2NiCl_2$, N-methylpyrrolidine, N-methylpyrrole, and $AlCl_3$ (ReagentPlus®) were purchased from Sigma-Aldrich and used as received. Complex **1** was synthesized according to the literature.[12]

Preparation of the Homogeneous Catalyst Compositions

$AlCl_3$ was weighed into a Schlenk tube and covered with solvent. The buffer was added, and the yellow solution was stirred until all aluminum chloride had dissolved. Subsequently, the nickel catalyst precursor was added to the Schlenk tube, and the solution was quickly syringed into the reaction vessel.

Synthesis of N-Methylpyrrolidine Hydrochloride

N-Methylpyrrolidine was dissolved in dry diethylether, and HCl gas was bubbled through the flask until no more gas was absorbed. The white, precipitated N-methylpyrrolidine

hydrochloride was filtered, washed three times with diethylether and *n*-pentane, dried in vacuo, and used without further purification.

Synthesis of the Ionic Liquid Catalyst Compositions

The ionic liquids were synthesized by directly mixing the corresponding amount of $AlCl_3$ and chloride salt in a cooled Schlenk tube. In the case of $EtAlCl_2$ containing systems, a 0.9 molar solution of $EtAlCl_2$ in heptane was added to the liquid, and the solvent was removed in vacuo. Few ml of an ionic liquid were filled into another Schlenk tube, and the corresponding amount of buffer was dissolved in the liquid by stirring. The nickel catalyst precursor was added from a freshly prepared stock solution in CH_2Cl_2, which was removed in vacuo afterwards. The obtained homogeneous solution was syringed into the reaction vessel. Its amount was determined by the weight difference of the syringe.

Procedure for Dimerization and Polymerization Reactions

For all dimerization and polymerization reactions, a stirred 300 ml Parr stainless steel autoclave was used. The steel vessel was kept in a drying oven at 150°C for several hours before an experiment.

Ethene: n-Heptane was added to the catalyst containing reactor vessel under argon counter flow. The system was put under vacuum, and the temperature was raised to 40°C. Then, an ethene pressure of 10 bar was applied. Cooling of the highly exothermic reaction was achieved manually by an external liquid nitrogen cooled acetone bath. After the experiment, the vessel was quickly cooled to –20°C. The pressure was released, the weight difference of the vessel was determined, and a cooled sample was directly analyzed by gas chromatography. The polyethylene was separated by filtration, washed several times with acetone and water, and its weight was determined after drying. The pure polyethylene samples obtained after filtration and drying were analyzed by differential scanning calorimetry and high temperature gel permeation chromatography.

Propene: The catalyst containing vessel was evacuated, and liquid propene (200 ml) was soaked into it at 77 K. The reaction was started by quickly heating the vessel to 40°C with boiling water. Cooling of the highly exothermic reaction was achieved manually by an external liquid nitrogen cooled acetone bath. After the experiment, the

vessel was cooled to 0°C, and the pressure was slowly released. After reaching ambient temperature, the weight gain of the vessel was determined, and the product phase was analyzed by gas chromatography. To determine the content of *n*-hexenes, 2-methylpentenes, and 2,3-dimethylbutenes, the product fraction was hydrogenated with palladium on activated carbon and analyzed by gas chromatography.

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8 Silica Supported Cocatalysts for Olefin Dimerization and Polymerization Reactions with Nickel Complexes

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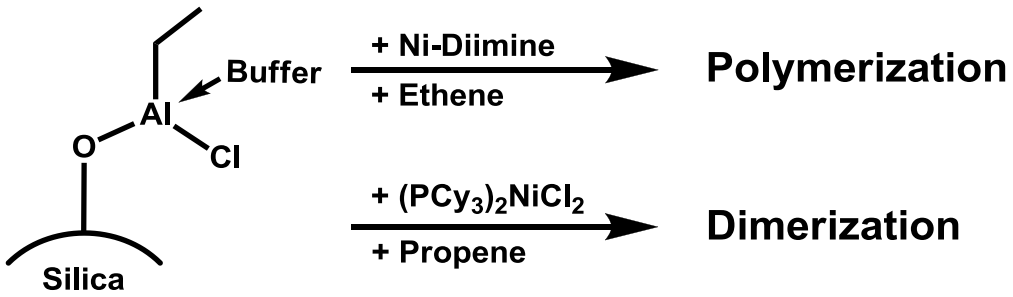


Abstract: We developed a new buffered silica based Lewis acid cocatalyst for olefin dimerization and polymerization reactions with nickel complexes. The Lewis acidities of $EtAlCl_2$ and Et_2AlCl modified silicas were adjusted by the addition of $BiPh_3$ or N-methylpyrrole buffers. The buffered heterogeneous cocatalysts were successfully employed to activate nickel complexes for selective propene dimerization reactions to give 91% dimers. Buffer addition also reduced the rate of ligand abstraction from the catalytically active nickel center. In combination with a nickel diimine complex, ethene was polymerized to give 69 wt% polyethylene and 31 wt% oligomers. The polyethylene displayed a molecular weight of 154 kg/mol and a PDI of 3.26. The oligomers consisted of 93% butenes, 46% thereof being 1-butene. Furthermore, triphenylbismuth buffered

Lewis acidic chloroaluminate ionic liquids were coated on surface modified silica to yield a supported ionic liquid phase (SILP) system. Dimer selectivities of up to 94% were obtained with the SILP system in nickel catalyzed propene dimerization reactions. The newly developed silica based cocatalysts provide promising new olefin dimerization systems suitable for fixed bed applications.

8.1 Introduction

Most of the major metal complex catalyzed olefin conversion processes including hydroformylation, metathesis, dimerization, and polymerization reactions were discovered in homogeneous solution. However, all of these processes were converted to biphasic[1] or heterogeneous[2] systems in order to improve the economics for their application in large scale industrial processes. Olefin polymerization reactions, which yield solid products, have to be performed in slurry, bulk-monomer, or gas-phase processes for large capacities.[2d] Therefore, the catalysts are usually supported on an inorganic carrier to prevent reactor fouling and to guarantee uniform polymer particle sizes.[2c, 2d] For example, the old heterogeneous Union Carbide (chromocene/silica) and Phillips (CrO_3/silica) catalysts are still responsible for about one third of the global HDPE production.[3] For olefin dimerization reactions, which yield gaseous or liquid products, heterogeneous catalyst systems are advantageous for fixed bed reactors because the do not require expensive technologies. The olefin stream passes the solid catalyst, which is immobilized in the reactor.

There are several different approaches to support metal complexes, which have to be activated by aluminum based cocatalysts for olefin dimerization or polymerization reactions. The most common method is the impregnation of an inorganic support material with alkylaluminum compounds like methylaluminoxane (MAO) or trimethyl-aluminum (TMA) and a metal complex.[2c, 2d, 4] However, the high prices of MAO and TMA restrict their use for the production of valuable high performance polymers. The well known titanium chloride based Ziegler-Natta catalysts supported on $MgCl_2$ also belong to this class.[3a, 5]

A second possibility is to connect metal complexes covalently to a heterogeneous support.[6] However, the attachment to support materials requires changes in the ligand structure and increased synthetic efforts.

Lewis acidic inorganic oxide materials provide an alternative to the above mentioned systems. McDaniel *et al.* developed a novel cocatalyst system for metallocene complexes based on alkylaluminum compounds and solid acids.[7] The surface of inorganic oxides was modified by high temperature treatment with chlorinated or fluorinated substrates. In combination with triethylaluminum, these solid Lewis acids are able to activate metallocene complexes for ethene polymerization reactions. This industrial research of ChevronPhillips Chemical[7] showed that it is desirable to develop heterogeneous cocatalysts, which can easily be synthesized, stored and used to activate common metal complexes feasible for olefin dimerization and polymerization reactions.

A lot of research has already been done on the surface modification of inorganic oxide materials. In particular, hydroxyl groups located at silica surfaces[8] can be modified with reactive aluminum compounds to yield strong heterogeneous Lewis acids. The strongest Lewis acid sites are obtained by treating silica with either $AlCl_3$[9] to release HCl or with $EtAlCl_2$[10] to release ethane. In the presence of both Al–Cl and Al–C bonds the latter preferentially react.[11] These materials catalyze cracking, disproportionation, or isomerization of alkanes as well as cationic oligomerization reactions of olefins.[10a] The acid strength of such grafted aluminum species usually increases with more halogen atoms being attached to the aluminum center.[12]

Since $SiO–AlCl_2$ surface groups initiate the above mentioned cationic olefin oligomerization reactions, they cannot be applied as cocatalysts for metal complex catalyzed olefin dimerization or polymerization reactions. First, the Lewis acidities of such strong solid acids have to be reduced to a level, at which said uncontrolled cationic olefin oligomerization reactions do not take place.

We identified new strategies to overcome this problem. In a recent paper, we described novel cocatalysts for nickel catalyzed olefin dimerization and polymerization reactions based on a combination of aluminum chloride and weak Lewis bases such as N-methylpyrrole or triphenylbismuth.[13] The weak Lewis bases buffered the high Lewis acidity of aluminum chloride and kept it in solution by forming a weak adduct. Such organic buffers were previously used by Wasserscheid *et al.*[14] and our group[15] to

reduce the “latent acidity”[16] of Lewis acidic chloroaluminate ionic liquids. The buffered chloroaluminate melts were employed to activate nickel complexes for selective dimerization reactions of α-olefins. Thus, we expected that the addition of these buffering substances would control the Lewis acidities of $EtAlCl_2$ modified solid acids in a similar manner. Nickel based systems are particularly interesting because they can be activated with cheap Et_2AlCl or $EtAlCl_2$ cocatalysts. Depending on the ligand structure, they were found to catalyze both selective olefin dimerization[17] or polymerization[18] reactions.

The second approach relied on silica treated with excess Et_2AlCl. Since the Lewis acidity of the surface aluminum species decreases with a decreasing number of halogens,[12] the substitution of $SiO–AlCl_2$ groups with SiO–AlEtCl should come along with reduced Lewis acidities. Because Et_2AlCl can react with both ethyl groups to release two molecules ethane per molecule Et_2AlCl,[11] the use of excess Et_2AlCl should favour the formation of SiO–AlEtCl species. Upon buffering with N-methylpyrrole and $BiPh_3$, these SiO–AlEtCl species were expected to activate nickel complexes for selective olefin dimerization and polymerization reactions. Furthermore, $EtAlCl_2$ modified silica should provide a suitable support material for buffered chloroaluminate ionic liquids to obtain pseudo heterogeneous supported ionic liquid phase[19] (SILP) dimerization systems.

8.2 Results and Discussion

Buffered Silica Supported $EtAlCl_2$ as Cocatalyst for Heterogeneous Nickel Catalyzed Propene Dimerization Reactions

For all experiments, Davicat® SI1102 silica with a particle size of 0.4 – 0.8 mm from W.R. Grace & Co. was used. It has a surface area of 311 m^2/g, a pore volume of 1.12 cm^3/g and a pore diameter of 144 Å. The silica was oven dried at 350°C prior to all manipulations. In a preliminary experiment, treatment of dehydrated silica with excess $EtAlCl_2$ resulted in a weight gain of about 15.7%. Under the approximation that each molecule of $EtAlCl_2$ reacted with only one surface OH group to release ethane,[11] the density of reactive surface OH groups was calculated to be 1.6 mmol/g.

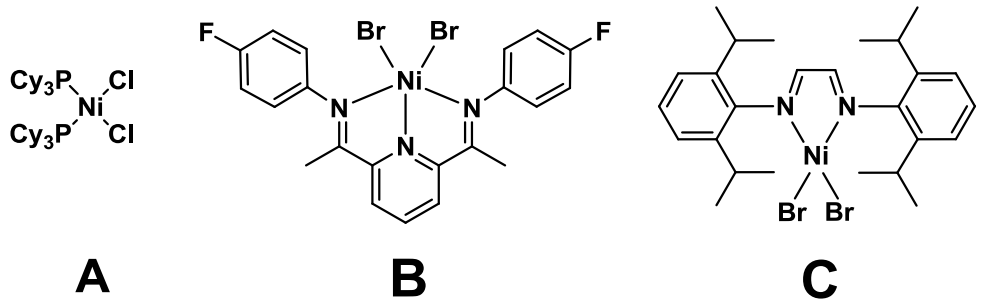
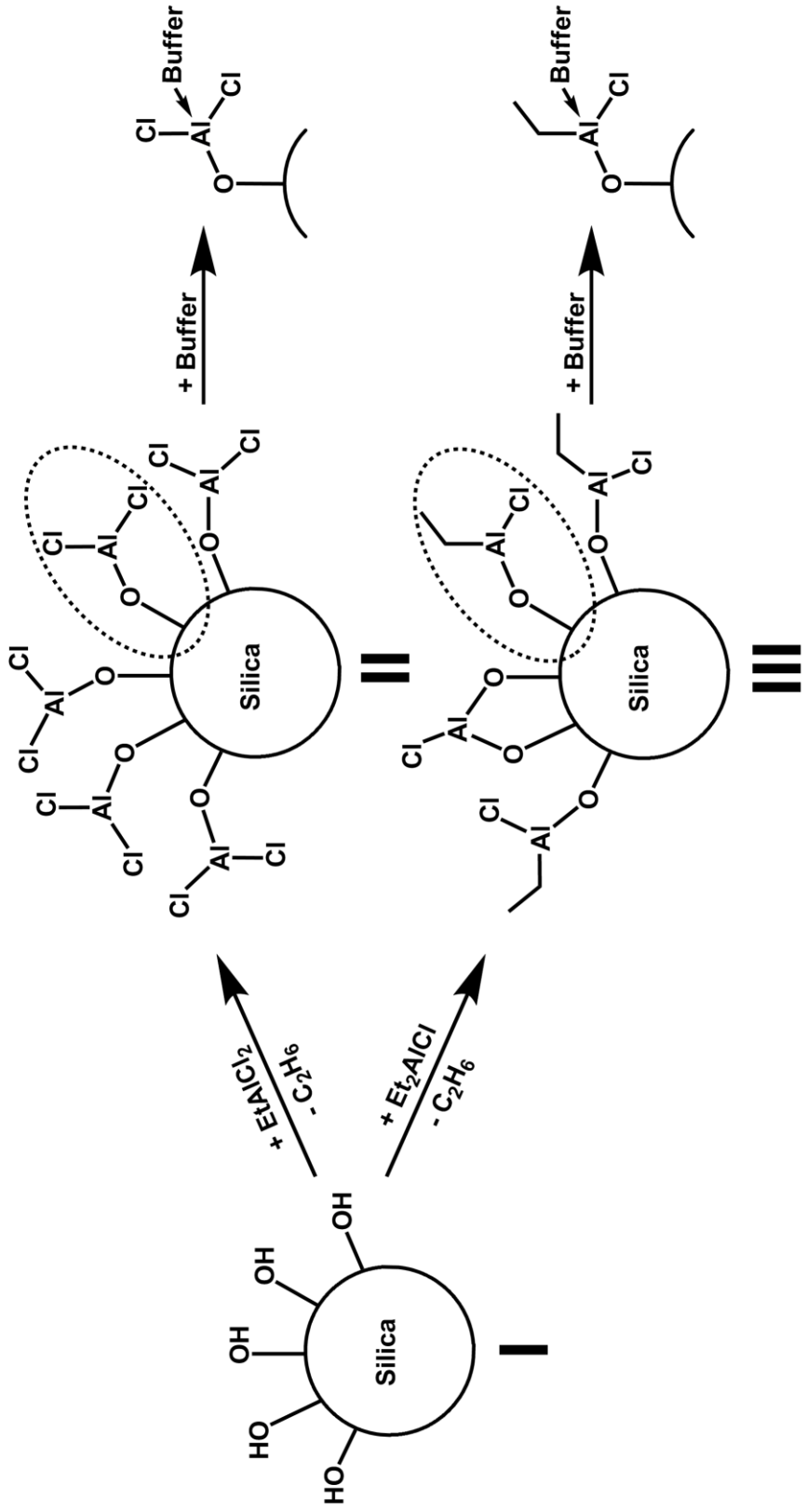


Figure 1: Catalyst precursors used for propene dimerization (**A**, **B**) and ethene polymerization reactions (**C**).

Scheme 1 shows the surface modification of dehydrated silica **I** with $EtAlCl_2$ and Et_2AlCl to give silica **II** and **III**, respectively. First, the highly acidic $EtAlCl_2$ modified silica **II** was buffered with N-methylpyrrole or $BiPh_3$ (**Table 1**) and applied as cocatalyst for nickel catalyzed propene dimerization reactions with complex **A** (**Figure 1**).

Both systems were tested in batch experiments with liquid propene. In order not to destroy the silica structure, stirring was avoided. Triphenylbismuth was dispersed from a methylene chloride solution, which was removed afterwards. Its high molecular weight required reduced loadings. In the case of N-methylpyrrole, a cosolvent had to be applied to obtain a homogeneous distribution of the volatile heterocyclic buffer.

In both experiments, dimers were produced with high activities. Also, the dimer fraction consisted of remarkable amounts of 60% (1) and 47% (2) of valuable 2,3-dimethylbutenes. Without the buffer, viscous oils consisting of higher oligomers from cationic propene oligomerization reactions were obtained. However, the selectivities to give dimers were poor. Also, the N-methylpyrrole buffered system 2 was inactive in a subsequent experiment. Consequently, the Lewis acidity was still too high. Higher amounts of buffer could further reduce the acidity. However, huge amounts of the heavy $BiPh_3$ would be necessary, while N-methylpyrrole systems deactivated quickly.



Scheme 1: Surface modification of dehydrated silica (**I**) with ethylaluminum dichloride (**II**) and diethylaluminum chloride (**III**) and buffering of the Lewis acidic surface aluminum species.

Table 1: Heterogeneous nickel catalyzed propene dimerization reactions with buffered silica supported $EtAlCl_2$ cocatalysts (silica **II**).[1]

No.	Buffer	Solvent	[Buffer] / Si–[OH][2]	C_6 [%]	HEX [%]	MP [%]	DMB [%]	Activity[3]
1	$BiPh_3$	–	0.5	62.8	6	34	60	2.19
2	N-MP	*n*-Heptane	1.1	82.9	10	43	47	1.30

[1] Reaction conditions: 3.12 g (1) and 5.28 g (2) modified silica II, catalyst precursor A; catalyst loading = 0.13 wt%; Si–[OH] / [Ni] = 750; T = 25°C; no stirring; t = 60 min; 300 ml glass autoclave; 50 ml liquid propene; HEX = *n*-hexenes; MP = 2-methylpentenes; DMB = 2,3-dimethylbutenes; N-MP = N-methylpyrrole. [2] OH surface density = 1.6 mmol/g; calculated from the weight gain upon the reaction of dehydrated silica with excess $EtAlCl_2$ under the assumption that each $EtAlCl_2$ molecule reacts with exactly one OH group to release ethane. [3] $t_{product}$ / mol_{Ni} x h.

Buffered Silica Supported Et_2AlCl as Cocatalyst for Heterogeneous Nickel Catalyzed Propene Dimerization Reactions

Now, excess Et_2AlCl was used instead of $EtAlCl_2$ to modify silica (**Scheme 1**). The obtained surface modified silica **III** was applied as cocatalyst for nickel catalyzed propene dimerization reactions (**Table 2**). Even without the addition of a buffer, 84% dimers were produced with complex **A**. The combination of silica **III** and complex **A** yielded a very stable propene dimerization system, which kept its selectivity and activity over at least three experiments (3a – c). Usually, the sterically demanding tricyclohexyl-phosphine ligands of complex **A** are responsible for the formation of highly branched 2,3-dimethylbutenes (DMB).[17, 20] However, the 2,3-dimethylbutene content of only 10% (3a) suggested that the Lewis acidity of the unbuffered silica **III** cocatalyst was responsible for the removal of the tricyclohexylphosphine ligands from the catalytically active nickel center. In the following two experiments, the DMB selectivities further dropped to 6% (3b) and 5% (3c). These were exactly the values described for ligand free nickel salts.[14d]

Further, the Et_2AlCl modified silica **III** system was buffered by the addition of small amounts of $BiPh_3$ (4) and N-methylpyrrole (5 – 9). The addition of 0.03 equivalents of $BiPh_3$ did not improve the dimer selectivities. However, the DMB content increased to

41% (4) compared to 10% of the unbuffered system (3a). Obviously, the interaction of $BiPh_3$ with the Lewis acidic surface aluminum species hindered the abstraction of tricyclohexylphosphine from the nickel complex, even if only small amounts of buffer were present. As expected for cocatalysts with lower Lewis acidities, the activity was lower compared to the unbuffered system.

Table 2: Heterogeneous nickel catalyzed propene dimerization reactions with buffered silica supported Et_2AlCl cocatalysts (silica **III**).[1]

No.	Buffer	Solvent	[Buffer] / Si–[OH][2]	C_6 [%]	HEX [%]	MP [%]	DMB [%]	Activity[3]
3a	–	–	–	84.4	25	65	10	1.47
3b	Subsequent Runs[4]			82.6	26	68	6	1.46
3c				81.2	27	68	5	1.36
4	$BiPh_3$	–	0.030	83.0	10	49	41	0.79
5	N-MP	*n*-Heptane	0.030	90.1	14	51	35	0.25
6	N-MP	*n*-Heptane	0.020	90.0	16	53	31	0.32
7	N-MP	*n*-Heptane	0.010	90.7	19	58	23	0.41
8	N-MP	*n*-Heptane	0.003	90.3	21	62	17	0.61
9	N-MP	Toluene	0.003	89.9	17	56	27	0.49

[1] Reaction conditions: 4.1 – 6.4 g modified silica III, catalyst precursor A; catalyst loading = 0.14 wt%; Si–[OH] / [Ni] = 675; T = 25°C; no stirring; t = 60 min; 300 ml glass autoclave; 20 ml solvent; 50 ml liquid propene; HEX = *n*-hexenes; MP = 2-methylpentenes; DMB = 2,3-dimethylbutenes; N-MP = N-methylpyrrole. [2] OH surface density = 1.6 mmol/g; calculated from the weight gain upon the reaction of dehydrated silica with excess $EtAlCl_2$ under the assumption that each $EtAlCl_2$ molecule reacts with exactly one OH group to release ethane. [3] $t_{product}$ / mol_{Ni} x h. [4] Products decanted after each run.

For N-methylpyrrole experiments, *n*-heptane was employed as cosolvent. The addition of 0.03 equivalents of N-methylpyrrole raised the dimer selectivity to 90% (5). The DMB content was in the range of the $BiPh_3$ buffered system (4). Surprisingly, the amount of

N-methylpyrrole could be reduced by a factor of ten, and the dimer selectivity remained at 90% (9). With 17%, the DMB content was still higher than in the unbuffered system (3a). Changing the solvent from *n*-heptane to toluene did not affect the dimer selectivity. However, the DMB content increased from 17% to 27%. This might be attributed to the additional π-interactions of toluene with the Lewis acidic aluminum sites.

Buffering Et_2AlCl modified silica cocatalysts with small amounts of Lewis bases provides a promising new olefin dimerization system suitable for fixed bed applications. The active cationic nickel species[21] should remain on the silica surface, while small amounts of buffer can be added to the olefin feed to maintain high selectivities. Cheap and nontoxic buffers like N-methylpyrrole could remain in the product fraction. No further purification would be necessary.

Buffered Silica Supported Et_2AlCl as Heterogeneous Cocatalyst for Nickel Catalyzed Ethene Polymerization Reactions

After nickel complexes were successfully activated to dimerize propene with buffered Et_2AlCl modified silica **III**, we extended our study for ethene polymerization reactions. Therefore, a Brookhart type nickel diimine complex **C** was employed as catalyst precursor (**Figure 1**) instead of complex **A**. The complex is known to polymerize ethene upon activation with MAO or Et_2AlCl.[18, 22] While propene dimerization reactions occurred even after the ligands were abstracted, the presence of the bulky diimine ligand is crucial for nickel based ethene polymerizations.[13] Thus, the experiment was performed in toluene applying 0.03 equivalents of N-methylpyrrole. Both compounds reduced the rates of ligand abstraction in previous propene dimerization reactions with complex **A**.

The system produced 69 wt% polymer and 31 wt% oligomers with an activity of 770 kg per mol nickel and hour (**Table 3**). Remarkably, 93% of the oligomers were butenes with a selectivity of 46% to give 1-butene. The polymer grew at the silica surface exclusively, no fouling could be observed. After washing and drying, free flowing polymer particles with a homogeneous size distribution were obtained. High temperature gel permeation chromatography of the polyethylene revealed a molecular weight of 154 kg/mol and a PDI of 3.26. Its degree of crystallinity was determined to 25%.

Table 3: Heterogeneous nickel catalyzed ethene polymerization reaction with a buffered silica supported Et_2AlCl cocatalyst (silica **III**).[1]

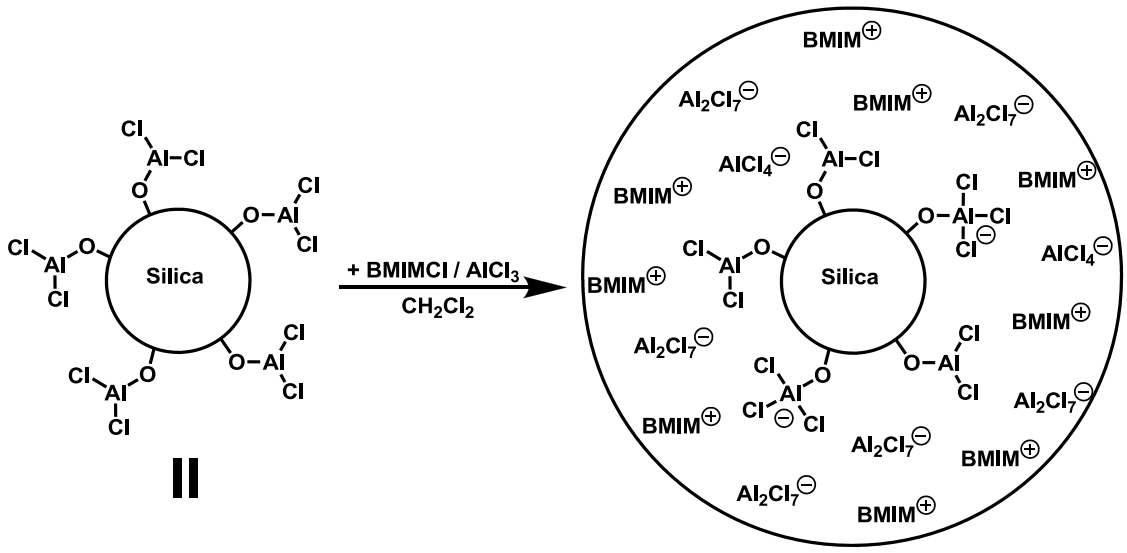
No.	Polymer [wt%]	M_w[2]	PDI	T_m [°C]	X_c [%][3]	Oligomers [wt%]	C_4 [%][4]	1-C_4 [%][5]	Activity[6]
10	69[7]	154	3.26	123.3	25	31	93.2	46.2	0.77

[1] Reaction conditions: 12.60 g modified silica III, catalyst precursor C; catalyst loading = 0.14 wt%; Si–[OH] / [Ni] = 600; Si–[OH] / [N-methylpyrrole] = 0.03; OH surface density = 1.6 mmol/g; calculated from the weight gain upon the reaction of dehydrated silica with excess $EtAlCl_2$ under the assumption that each $EtAlCl_2$ molecule reacts with exactly one OH group to release ethane; T = 40°C; stirring rate = 600 min^{-1}; t = 60 min; stirred 300 ml Parr stainless steel autoclave; 70 ml toluene; 10 bar ethene. [2] kg/mol. [3] Crystallinity calculated with ΔH_m = 293 J/g for 100% crystalline PE. [4] Molar amount of butenes within oligomer fraction. [5] Molar amount of 1-butene within butenes. [6] $t_{product}$ / mol_{Ni} x h. [7] 127 wt% polymer on silica.

The exclusive growth of the polymer chains on the silica particles indicated that the active species were immobilized on the surface. As soon as a diimine ligand was abstracted, the active nickel catalyst switched from selective ethene polymerization to ethene dimerization. At higher buffer levels and optimized reaction conditions, the amount of polyethylenes could certainly be further increased.

Silica Supported Triphenylbismuth Buffered Chloroaluminate Ionic Liquid Cocatalysts for Heterogeneous Nickel Catalyzed Propene Dimerization Reactions

Finally, a triphenylbismuth buffered 1-butyl-3-methylimidazolium (BMIM) chloroaluminate ionic liquid was coated on dehydrated and surface modified silica **I** and silica **II**, respectively. Such $BiPh_3$ buffered chloroaluminate melts were found to be efficient solvents and cocatalysts for biphasic, nickel catalyzed olefin dimerization reactions.[15] The concept of supported ionic liquid phases (SILP) was introduced by Wasserscheid *et al.*[19] A thin film of a catalytically active ionic liquid coated on porous support materials combines the advantages of biphasic and heterogeneous catalysis. For example, acidic chloroaluminates were supported on inorganic oxide materials and used for Friedel Crafts alkylation reactions.[23] Supported buffered chloroaluminate ionic liquid cocatalysts for nickel catalyzed olefin dimerization reactions have not been reported yet.



Scheme 2: Supporting of BMIM chloroaluminate on surface modified silica **II**.

The triphenylbismuth buffer was predestined for such an application since it remained in the ionic liquids yielding stable biphasic dimerization systems.[15a, 15c] Therefore, $BiPh_3$ buffered 1-butyl-3-methylimidazolium chloroaluminate melts were supported on silicas **I** and **II** in various compositions. The obtained granular powders with different loadings were used as cocatalysts for batch propene dimerization reactions with catalyst precursor **A** (**Table 4**). The coating was achieved by removing methylene chloride from a suspension of buffered ionic liquid and the corresponding amount of silica (**Scheme 2**).

First, dehydrated silica **I** was used as support material for $[BMIM]^+[Al_2Cl_7]^-$ with a $BiPh_3$ content of 0.60 equivalents relative to the cation. In a biphasic reaction, this composition yielded 91% dimers with complex **B**.[15c] With a loading of 200 wt% ionic liquid, the system became greasy (11), while a free flowing powder was obtained with 150 wt% (12). However, both experiments showed low activities and selectivities. Obviously, the resulting supported systems displayed increased Lewis acidities compared to their biphasic equivalents. Presumably, $AlCl_3$ reacted with surface hydroxyl groups to give highly Lewis acidic $SiO–AlCl_2$ species. The HCl produced from this reaction also leads to the formation of superacidic protons.[24] The $SiO–AlCl_2$ groups probably also act as chloride acceptors binding a certain amount of BMIMCl. Therefore, even higher amounts of $BiPh_3$ would be necessary to obtain satisfactory dimer selectivities.

Table 4: Nickel catalyzed propene dimerization reactions with $BiPh_3$ buffered 1-butyl-3-methylimidazolium (BMIM) chloroaluminate ionic liquids supported on silica.[1]

No.	$[AlCl_3]$ / [BMIMCl]	$[BiPh_3]$ / [BMIMCl]	Silica	IL Loading [wt%]	Productivity[2]	C_6 [%]
11	2.00	0.60	I	200	3.8	72.1
12	2.00	0.60	I	150	2.2	Oil[3]
13	2.00	0.60	II	120	4.3	82.9
14	2.00	0.60	II	100	5.4	89.5
15	2.00	0.45	II	100	7.0	67.5
16	2.00	0.30	II	100	7.0	65.6
17	2.00	0.60	II	80	6.5	Oil[3]
18	2.00	1.00	II	80	4.9	89.6
19a	1.50	0.60	II	100	1.8	94.2
19b					1.6	93.0
19c					2.0	92.2
19d			Subsequent Runs[4]		2.5	88.3
19e					2.6	89.9
19f					2.8	85.0
19g					3.2	80.4

[1] Reaction conditions: 2.7 – 3.8 g buffered ionic liquid, catalyst precursor B; [cat] = 10^{-5} mol / $g_{ionic\ liquid}$; T = 25°C; no stirring; t = 60 min; 300 ml glass autoclave; 50 ml liquid propene; BMIM = 1-butyl-3-methylimidazolium; IL = ionic liquid. [2] $g_{product}$ / $g_{ionic\ liquid}$ x h. [3] Higher oligomers derived from a cationic oligomerization reaction. [4] Products decanted after each run.

Hence, $EtAlCl_2$ pre-treated silica **II** was tested as support material (13 – 19). The highest possible loading of systems supported on silica **II** was 120 wt% (13). At higher loadings, the system became greasy. With said 120 wt% loading, 83% dimers were obtained. At an ionic liquid loading of 100 wt% applying 0.60 equivalents of $BiPh_3$ buffer,

the dimer yield increased to 90% (14), which was similar to the unsupported system. With a reduced loading of 80 wt%, mainly higher oligomers were obtained (17). For this system loaded with 80 wt% buffered $[BMIM]^+[Al_2Cl_7]^-$ ionic liquid, a buffer content of one equivalent was necessary to raise the dimer selectivity to 90% again (18).

Triphenylbismuth equalled about 37 wt% of the total weight in $[BMIM]^+[Al_2Cl_7]^-$ / $BiPh_3$ = 0.60 systems. With one equivalent of buffer, even 50 wt% of the catalytically active melt consisted of $BiPh_3$. Therefore, small changes in terms of loading or composition led to drastic changes in performance. For ionic liquids derived from cations with lower molecular weights, lower loadings would certainly be sufficient. A system with a less acidic composition of $[AlCl_3]$ / [BMIMCl] = 1.50 and 0.60 equivalents of $BiPh_3$ yielded 94% dimers in the first experiment (19a). Then, the products were decanted, and the batch experiment was repeated. In four subsequent catalytic runs, the system maintained a dimer selectivity of around 90% (19b – e) before it dropped significantly.

All systems displayed low productivities compared to their biphasic analogues.[15c] However, no stirring was applied in order not to destroy the silica structure. With an improved mixing, the productivities could certainly be increased. The reference complex **B** had no effect on the branching of the hexene dimers,[15a] all C_6 fractions consisted of (± 2%) 25% *n*-hexenes, 69% 2-methylpentenes, and 6% 2,3-dimethylbutenes. This correlated to the typical product distribution obtained from ligand free nickel salts.[14d]

Triphenylbismuth buffered chloroaluminate ionic liquids supported on surface modified silica provide novel heterogeneous cocatalyst systems for nickel catalyzed olefin dimerization reactions. If ionic liquids based on amine hydrochlorides are used, both the buffer and the amine can be recovered by a simple acid base extraction.[15a] Especially the application for gas phase ethene dimerization reactions is very promising since no leaching of either the ionic liquid or the buffer can occur. Furthermore, alkylaluminum free ionic liquid compositions are less sensitive to oxygen or polar impurities.

Conclusion

We developed a new class of buffered solid acid cocatalysts for nickel catalyzed olefin dimerization and polymerization reactions. The Lewis acidity of $EtAlCl_2$ modified silica was reduced by the addition of $BiPh_3$ or N-methylpyrrole buffers. Uncontrolled cationic

olefin oligomerization reactions, which usually occur in the presence of $SiO–AlCl_2$ species, were suppressed by the donor-acceptor interactions.

Silica modification with Et_2AlCl instead of $EtAlCl_2$ yielded solid cocatalysts with reduced Lewis acidities. The cocatalysts were successfully employed to activate a nickel complex for selective propene dimerization reactions to give 84% dimers. The addition of small amounts of N-methylpyrrole to the catalyst suspension increased the dimer selectivity up to 91%. Furthermore, the addition of either $BiPh_3$ or N-methylpyrrole hindered the ligand abstraction from the catalytically active metal center. The same Et_2AlCl modified silica with additional N-methylpyrrole buffer was used to activate a nickel diimine complex for ethene polymerization reactions to give 69 wt% polyethylene and 31 wt% oligomers. Remarkably, 93% of the oligomers were butenes with 46% thereof being 1-butene. The polyethylene was partially crystalline and displayed a molecular weight of 154 kg/mol with a PDI of 3.26.

Buffered, surface modified silicas provide a promising new class of cocatalysts for heterogeneous nickel catalyzed olefin dimerization and polymerization reactions. Surface modification was accomplished in one step with cheap Et_2AlCl. The heterogeneous cocatalysts were able to activate common nickel complexes and can be applied in fixed bed tubes for olefin dimerization reactions. Selectivity control could be achieved by the addition of small amounts of an N-methylpyrrole buffer to the olefin feed stream. In combination with nickel based polymerization catalysts, the same systems could be applied in slurry ethene polymerization reactions. Our results indicated that the catalytically active species were immobilized on the silica surface.

Finally, $BiPh_3$ buffered Lewis acidic chloroaluminate ionic liquids were coated on surface modified silicas to yield supported ionic liquid phase (SILP) systems for nickel catalyzed propene dimerization reactions. Dimer selectivities up to 94% were obtained with the SILP systems. In contrast to the above mentioned buffered surface modified silica cocatalysts, no external buffer had to be added. The $BiPh_3$ buffer was immobilized in the ionic liquid. Such SILP systems are predestined for gas phase ethene dimerization reactions since no leaching can occur in gas phase reactions.

8.3 Experimental Section

General Information

All chemical manipulations were carried out using standard Schlenk techniques under argon atmosphere. *n*-Heptane and *n*-pentane were distilled from Na/K alloy under inert atmosphere. Methylene chloride was distilled in two steps from P_4O_{10} and CaH_2, toluene from P_4O_{10} and Na/K alloy. The products of the dimerization experiments were characterized by gas chromatography (Agilent 6850) and GC-MS (FOCUS DSQ™ Thermo Scientific). Differential scanning calorimetry experiments were conducted at a heating rate of 10°C/min under N_2 atmosphere with a Perkin-Elmer Diamond DSC, calibrated with indium. The endothermic maximum of the second heating cycle was taken as T_m. The molecular weights (M_w/M_n) of the ethylene polymers were determined by gel permeation chromatography on a Polymer Laboratories Ltd. (PL-GPC220) chromatograph at 150°C using 1,2,4-trichlorobenzene as the mobile phase. The sample was prepared by dissolving the polymer (0.1% weight/volume) in the mobile phase solvent in an external oven and was run without filtration. The molecular weight was referenced to polystyrene (M_w = 510 – 3100000 g/mol) standards using the universal calibration method.[25] The reported values are the average of at least two independent determinations. Ethene (99.9%) and propene (99.3%) were purchased from Riessner Gase, Lichtenfels, and were dried over a column packed with P_4O_{10}. $EtAlCl_2$ (1.8 N in toluene) and Et_2AlCl (0.9 N in toluene) were purchased from Acros. Triphenylphosphine and triphenylbismuth were purchased from ABCR. N-Methylpyrrole, 1-butyl-3-methylimidazolium tetrachloroaluminate (BASF), $AlCl_3$ (ReagentPlus®), and $(PPh_3)_2NiCl_2$ were purchased from Sigma-Aldrich and used as received. Complexes **A**[15a] and **C**[18] were synthesized according to the literature.

Preparation of the Surface Modified Silicas II and III

For all experiments, Davicat® SI1102 silica with a particle size of 0.4 – 0.8 mm from W.R. Grace & Co. was used. It has a surface area of 311 m^2/g, a pore volume of 1.12 cm^3/g and a pore diameter of 144 Å. Prior to all manipulations, the silica was dehydrated for 4 hours at 350°C to give silica **I**. The dehydrated silica **I** was filled into a glass frit under argon counter flow, and half of its volume was covered with toluene. For

silica **II**, 2 mmol $EtAlCl_2$ (1.8 N in toluene) per g, for silica **III** 3 mmol Et_2AlCl (0.9 N in toluene) per g were added. The frit was equipped with a pressure valve, and the suspension was stirred with a spatula once in a while. The mixture was left standing over night until no more bubbles could be observed. The modified silica was washed three times with toluene and *n*-pentane, dried in vacuo, and stored in a Schlenk tube.

Preparation of Buffered Surface Modified Silica Cocatalyst Compositions

The corresponding amount of surface modified silica was weighed into a glass autoclave. For $BiPh_3$ buffered systems (1, 4), the silica was covered with CH_2Cl_2. Then, the buffer was added, and the autoclave was gyrated. To the CH_2Cl_2 suspension the catalyst precursor **A** was added from a stock solution in CH_2Cl_2. Subsequently, the methylene chloride was removed in vacuo to yield the heterogeneous $BiPh_3$ buffered propene dimerization system. For the unbuffered experiment (3), the same procedure was applied without the addition of $BiPh_3$.

For N-methylpyrrole buffered systems (2, 5 – 9), the silica was covered with *n*-heptane or toluene. The corresponding amount of N-methylpyrrole was added to the suspension. For the experiments in **Table 2**, a dilution series of N-methylpyrrole in *n*-heptane and toluene was performed. The autoclave was gyrated and left standing for a few minutes. Then, the solid catalyst precursor **A** was added. After it had dissolved, the system was used for heterogeneous N-methylpyrrole buffered propene dimerization reactions.

Preparation of Triphenylbismuth Buffered 1-Butyl-3-methylimidazolium Chloroaluminate Ionic Liquid Supported on Silica

$AlCl_3$ was dissolved in commercial 1-butyl-3-methylimidazolium tetrachloroaluminate to obtain the desired compositions. The corresponding amounts of ionic liquid and $BiPh_3$ were added to a glass autoclave and mixed until a homogeneous solution was obtained. Subsequently, the buffered ionic liquid was diluted with CH_2Cl_2 and silica was added followed by the addition of catalyst precursor **B**. Upon its dissolution, the solvent was removed in vacuo to yield a free flowing granular powder.

Procedure for Propene Dimerization Reactions with Heterogeneous Catalysts (Experiments 1 – 9, 11 – 19)

For all propene dimerization reactions, a 300 ml glass autoclave was used. No stirring was applied in order not to destroy the silica structure and to guarantee identical conditions. The glass vessel was kept in a drying oven at 150°C for several hours before an experiment.

An autoclave containing the heterogeneous catalyst composition was cooled, and vacuum was applied. Subsequently, propene (50 ml) was condensed into the glass autoclave by liquid nitrogen cooling. Then, the autoclave was placed in a metal box for safety reasons, and the temperature was regulated by an external water bath. After the experiment, the pressure was slowly released by opening a valve. After reaching ambient temperature, the weight difference of the autoclave was determined, and the product phase was analyzed by gas chromatography. To determine the content of *n*-hexenes, 2-methylpentenes, and 2,3-dimethylbutenes, the product fraction was hydrogenated with palladium on activated carbon, and the products were analyzed by gas chromatography. In the case of experiments 3 and 19, the product phase was decanted, analyzed by gas chromatography, and the experiment was repeated.

Procedure for Ethene Polymerization Reactions with an N-Methylpyrrole Buffered Surface Modified Silica Cocatalyst (Experiment 10)

For the ethene polymerization reaction, a stirred 300 ml Parr stainless steel autoclave was used. The steel vessel was kept in a drying oven at 150°C for several hours before an experiment, and it was filled with argon. The autoclave was cooled to 0°C with an ice bath. Then, a solution of N-methylpyrrole (0.05 ml) in toluene (50 ml) was added to the reactor followed by the addition of surface modified silica **III** (12.60 g). Complex **C** (18.0 mg) was suspended in toluene (20 ml), and the suspension was filled into the reactor. The system was put under vacuum, and the temperature was raised to 40°C. Then, after 5 minutes of stirring, an ethene pressure of 10 bar was applied. Cooling of the exothermic reaction was achieved manually by an ice bath. After the experiment, the vessel was quickly cooled to –20°C. The pressure was released, the weight difference of the vessel was determined (23.24 g), and a cooled sample was directly analyzed by gas chromatography. The silica / polyethylene composite material was separated by filtration, washed several times with acetone and water, and its weight was determined after

drying (28.62 g silica + polyethylene). A sample of the composite material was stirred for 2 hours in 1,2,4-trichlorobenzene at 120°C to dissolve the polyethylene. The viscous solution was quickly filtered, and the polymer was precipitated by the addition of acetone. The pure polyethylene sample obtained after filtration and drying was analyzed by differential scanning calorimetry and high temperature gel permeation chromatography.

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9 Solubility Behaviour of $TiCl_4$, $ZrCl_4$, and $HfCl_4$ in Chloroaluminate Ionic Liquids

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Abstract: The solubility of $NbCl_5$, $TaCl_5$, $TiCl_4$, $ZrCl_4$, and $HfCl_4$ in neutral [BMIM][$AlCl_4$] (BMIM = 1-butyl-3-methylimidazolium) was determined. While $TiCl_4$ was immiscible with the neutral ionic liquid, 0.80 molar equivalents of $ZrCl_4$ and stoichiometric amounts of $HfCl_4$ dissolved in the melt at ambient temperature. The crystal structures and the unit cell parameters of $[Ti_2Cl_{10}][BMIM]_2$, $[Zr_2Cl_{10}][BMIM]_2$, and $[Hf_2Cl_9][PhNMe_3]$ were determined. $[Ti_2Cl_{10}][BMIM]_2$, and $[Zr_2Cl_{10}][BMIM]_2$ were crystallized from basic chloroaluminate melts. With a trimethylanilinium cation, $[Hf_2Cl_9][PhNMe_3]$ crystallized from an equimolar composition of $PhNMe_3Cl$, $AlCl_3$, and $HfCl_4$ abstracting a chloride ligand from $[AlCl_4]^-$ to give highly Lewis acidic $[Al_2Cl_7]^-$ anions.

9.1 Introduction

About 30 years ago, Wilkes *et al.* and Osteryoung *et al.* reported the first room temperature ionic liquids based on aluminum chloride.[1] In combination with organic cations like N-alkylpyridinium or 1-alkyl-3-methylimidazolium chloride, $AlCl_3$ formed liquids at ambient temperature over a wide range of compositions. For example, a

mixture of 1-ethyl-3-methylimidazolium chloride with two equivalents of $AlCl_3$ was still found to be a liquid at – 80°C.[2]

The Lewis acidities of such chloroaluminate ionic liquids are determined by the ratio of $AlCl_3$ to organic chloride salt.[3] In mixtures containing excess chloride salt, the $[AlCl_4]^-$ anion is the dominant aluminum species.[3] With increasing $AlCl_3$ content, the equilibrium is shifted towards $[Al_2Cl_7]^-$ species.[1a, 1c, 4] The presence of $[Al_3Cl_{10}]^-$ was also detected in highly acidic melts.[5] Usually, the melting points display a minimum with a ratio $AlCl_3$ / halide salt = 0.33 or 0.67, while a local maximum is observed for neutral compositions.[2a, 6]

Later, chloroaluminate ionic liquids were also employed as solvents for other metal salts.[7] Especially basic melts with free chloride ligands dissolved a variety of metal halides to give anionic chlorometallate complexes.[8] Acidic chloroaluminate melts were used to dissolve small amounts of titanium tetrachloride. The mixtures were used for electrochemical oxidation and metal deposition reactions.[9] Titanium and zirconium tetrachloride additives in acidic chloroaluminate melts were reported to promote alkylation reactions of isoparaffins with olefins.[10] Imidazolium cations were also applied for the formation of ionic liquids with a variety of other metal chlorides other than aluminum chloride.[11] However, the quantitative solubility behaviour of Lewis acidic metal chlorides in neutral tetrachloroaluminate melts has not been investigated yet.

9.2 Results and Discussion

Cationic Propene Oligomerization Reactions Initiated by Mixtures of Metal Chlorides and [BMIM][$AlCl_4$]

We were interested in new Lewis acidic ionic liquid compositions, which catalyze reactions typical for acidic chloroaluminate ionic liquids like cationic oligomerization of olefins,[12] isomerization[13] and cracking[14] reactions of saturated alkanes, or Friedel Crafts alkylation reactions.[15]

Therefore, we chose the commercially available 1-butyl-3-methylimidazolium (BMIM) tetrachloroaluminate as standard solvent for preliminary experiments with different metal chlorides. This neutral ionic liquid itself did not catalyze cationic olefin oligo-

merization reactions. In combination with 0.2 equivalents of $MgCl_2$, $LaCl_3$, $TiCl_4$, VCl_3, $CrCl_2$, $CrCl_3$, $MoCl_5$, WCl_4, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, CuCl, $CuCl_2$, $ZnCl_2$, BBr_3, $SiCl_4$, $SnCl_4$, PCl_5, or $BiCl_3$, no propene oligomers could be obtained. Yet, after the addition of 0.2 equivalents of $ZrCl_4$, $HfCl_4$, $NbCl_5$, or $TaCl_5$, the resulting mixtures were sufficiently acidic to catalyze cationic propene oligomerization reactions at ambient temperature to give viscous oils. The same behaviour was reported for ionic liquids containing excess aluminum chloride.[12, 16] Ionic liquids solely based on $NbCl_5$,[17] $TaCl_5$,[18] $TiCl_4$,[19] $ZrCl_4$,[20] or $HfCl_4$[21] were already reported. However, their mixtures with neutral chloroaluminate melts have not been described yet. Thus, the combination of these metal chlorides and neutral chloroaluminate melts might provide Lewis acids with novel properties compared to common ionic liquids exclusively based on $AlCl_3$.

Solubility of $TiCl_4$, $ZrCl_4$, $HfCl_4$, $NbCl_5$, and $TaCl_5$ in Neutral [BMIM][$AlCl_4$]

The solubility of selected metal chlorides in [BMIM][$AlCl_4$] at 298 K was quantified (**Table 1**). Therefore, to a certain amount of the corresponding chloride salt, neutral [BMIM][$AlCl_4$] was added and the mixture was heated until a homogeneous solution was obtained. Then, the warm solution was left standing for two days. This procedure was repeated until no more solid precipitated.

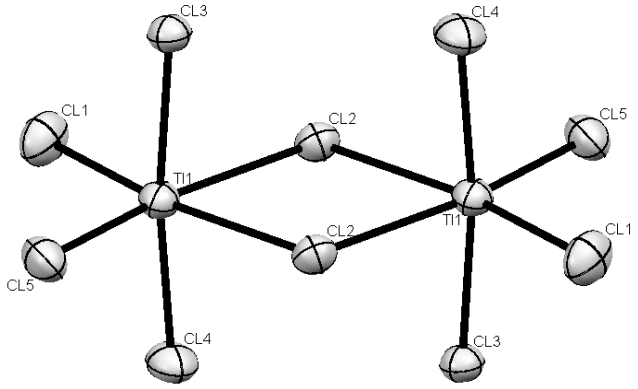
Table 1: Solubilities of different metal chlorides in neutral [BMIM][$AlCl_4$] at 298 K.

No.	Metal Chloride Additive	[Metal Chloride] / [BMIMCl][$AlCl_4$]
1	$AlCl_3$	1.0
2	$NbCl_5$	0.1
3	$TaCl_5$	0.2
4	$TiCl_4$	Immiscible
5	$ZrCl_4$	0.8
6	$HfCl_4$	1.0

The saturation concentrations of $NbCl_5$ and $TaCl_5$ were rather low with 10 (2) and 20 mol% (3) relative to the molar amount of BMIMCl. Titanium tetrachloride did not mix with the ionic liquid. Instead, a biphasic system was obtained with $TiCl_4$ forming the bottom phase (4). Surprisingly, large amounts of $ZrCl_4$ and $HfCl_4$ remained dissolved in [BMIM][$AlCl_4$]. Saturation of $ZrCl_4$ was reached at 0.8 equivalents (5). In the case of $HfCl_4$, even 100 mol% could be added (6). Thus, the molten salt systems consisted of more than 72 wt% $AlCl_3$ and $HfCl_4$.

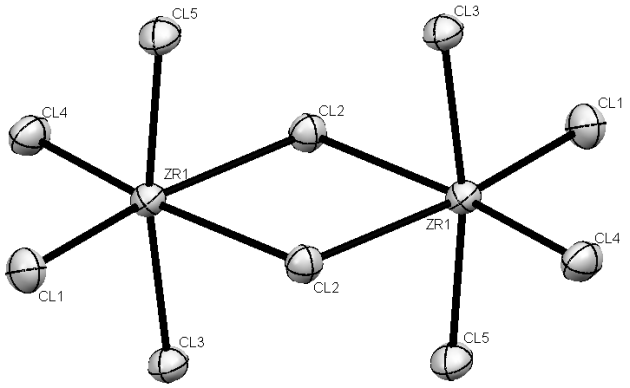
Crystal Structures of $[Ti_2Cl_{10}][BMIM]_2$, $[Zr_2Cl_{10}][BMIM]_2$, and $[Hf_2Cl_9][PhNMe_3]$

Further, we tried to crystallize some chlorometallate species of group IV metals from chloroaluminate melts. Due to its immiscibility with the neutral melt, a basic melt with $AlCl_3$ / BMIMCl = 0.5 was mixed with $TiCl_4$ and heated to yield a composition of [$AlCl_3$ = $TiCl_4$] / BMIMCl = 0.5 / 1.0. Upon cooling, $[Ti_2Cl_{10}][BMIM]_2$ crystallized leaving [BMIM][$AlCl_4$] as mother liquor. The binuclear $[Ti_2Cl_{10}]^{2-}$ anion consists of two titanium centers, each surrounded with six octahedrally coordinated chloride ligands connected by shared vertices (**Scheme 1**).



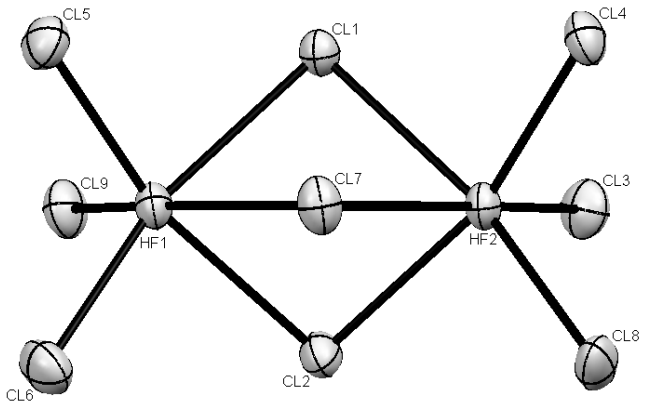
Scheme 1: ORTEP view of the $[Ti_2Cl_{10}]^{2-}$ anion in the crystal structure of $[Ti_2Cl_{10}][BMIM]_2$ (thermal ellipsoids were scaled to include 40% probability).

$[Zr_2Cl_{10}][BMIM]_2$ crystallized from both BMIMCl / $AlCl_3$ / $ZrCl_4$ = 1.0 / 0.6 / 0.4 and BMIMCl / $AlCl_3$ / $ZrCl_4$ = 1.0 / 0.8 / 0.4 melts. In neutral [BMIM][$AlCl_4$] systems, no crystallization occurred with 0.80 equivalents of $ZrCl_4$. Similar to $[Ti_2Cl_{10}]^{2-}$, the di-octahedral zirconium units share a vertex to form $[Zr_2Cl_{10}]^{2-}$ (**Scheme 2**).



Scheme 2: ORTEP view of the $[Zr_2Cl_{10}]^{2-}$ anion in the crystal structure of $[Zr_2Cl_{10}][BMIM]_2$ (thermal ellipsoids were scaled to include 40% probability).

Because the mixture of $[BMIM][AlCl_4]$ with one equivalent of $HfCl_4$ also did not crystallize, the cation was changed to trimethylphenylammonium. Subsequently, $[Hf_2Cl_9][PhNMe_3]$ crystallized from a melt with equimolar amounts of $PhNMe_3Cl$, $AlCl_3$, and $HfCl_4$. If all hafnium precipitated, the remaining solution would consist of $[Al_2Cl_7][PhNMe_3]$. Thus, $HfCl_4$ was sufficiently Lewis acidic to take off chloride ligands from $[AlCl_4]^-$ to give $[Al_2Cl_7]^-$ anions. The lack of chloride ligands prevented the formation of $[Hf_2Cl_{10}]^-$ anions leading to less saturated $[Hf_2Cl_9]^-$ anions (**Scheme 3**). Again, the metal center displayed an octahedral surrounding of chloride ligands. However, two octahedra were connected by shared faces.



Scheme 3: ORTEP view of the $[Hf_2Cl_9]^-$ anion in the crystal structure of $[Hf_2Cl_9][PhNMe_3]$ (thermal ellipsoids were scaled to include 40% probability).

This might explain the high solubilities and Lewis acidities of $ZrCl_4$ and $HfCl_4$ in [BMIM][$AlCl_4$] melts, in which highly Lewis acidic $[Al_2Cl_7]^-$ ions are present as well as $[M_2Cl_9]^{2-}$ ions (M = Zr, Hf). Its higher solubility indicated that $HfCl_4$ was able to abstract chloride ions to form $[Al_2Cl_7]^-$ to a greater extent than $ZrCl_4$.

Table 2: Selected bond lengths [Å] and angles [°] for the anions in the crystal structures of $[Ti_2Cl_{10}][BMIM]_2$, $[Zr_2Cl_{10}][BMIM]_2$, and $[Hf_2Cl_9][PhNMe_3]$.

	$[Ti_2Cl_{10}]^{2-}$	$[Zr_2Cl_{10}]^{2-}$		$[Hf_2Cl_9]^-$
M–M	3.887(1)	4.0408(1)	Hf–Hf	3.5764(2)
M–Cl_{br}	2.515(1)	2.6234(1)	Hf–Cl_{br}	2.6009(1)
M–Cl_{ax}	2.277(1)	2.4385(1)	Hf–Cl	2.3320(1)
M–Cl_{eq}	2.248(1)	2.3775(1)	Cl_{br}–Hf–Cl'_{br}	77.94
Cl_{br}–M–Cl'_{br}	78.64(2)	79.52	Cl_{br}–Hf–Cl(*cis*)	90.46
Cl_{br}–M–Cl_{ax}	87.91(3)	86.48	Cl_{br}–Hf–Cl(*trans*)	166.67
Cl_{br}–M–Cl_{eq}(*cis*)	89.31(3)	90.92	Cl–Hf–Cl'	100.38
Cl_{br}–M–Cl_{eq}(*trans*)	169.54(3)	169.74	Hf–Cl_{br}–Hf	87.08
Cl_{ax}–M–Cl_{eq}	92.08(3)	91.77		
Cl_{ax}–M–Cl'_{ax}	172.84(3)	170.37		
Cl_{eq}–M–Cl'_{eq}	101.13(3)	99.34		
M–Cl_{br}–M	101.36(3)	100.48		

The complex anions $[Ti_2Cl_{10}]^{2-}$, $[Zr_2Cl_{10}]^{2-}$, and $[Hf_2Cl_9]^-$ were already reported. For example, they can be prepared directly from the chloride salt mixed with corresponding amounts of a chloride source.[19b, 19c, 21-22] These structures can be considered as solid state structures of the corresponding metal chlorides with additional stabilizing chloride ligands.[22a] However, the crystal structures crystallized with $[BMIM]^+$ and $[PhNMe_3]^+$ cations were not measured yet. Also, the formation of these anions in the presence of saturated $[AlCl_4]^-$ ions was surprising.

Table 3: Crystal data and structure refinement of $[Ti_2Cl_{10}][BMIM]_2$, $[Zr_2Cl_{10}][BMIM]_2$, and $[Hf_2Cl_9][PhNMe_3]$.

Formula	$C_{16}H_{30}Cl_{10}N_4Ti_2$	$C_{16}H_{30}Cl_{10}N_4Zr_2$	$C_9H_{14}Cl_9NHf_2$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P $2_1/n$	P $2_1/n$	P $2_1/c$
a /Å	10.440(5)	16.9268(4)	15.1330(8)
b /Å	12.496(5)	10.6274(3)	10.7960(5)
c / Å	11.537(5)	35.0041(10)	13.8350(6)
α /deg	90	90	90
β /deg	90.150(5)	96.437(2)	109.349(5)
γ /deg	90	90	90
V /Å^3	1505.1(11)	6257.1(3)	2132.64(18)
Z	4	8	4
Crystal size /mm	0.97×0.70×0.58	0.57×0.22×0.22	0.67×0.55×0.35
D_{calcd} /g·cm^{-3}	1.599	1.731	2.530
μ /mm^{-1} (Mo K_α)	1.432	1.534	10.847
T /K	133(2)	133(2)	133(2)
θ-Range /deg	2.40–25.62	1.17–25.64	1.43–25.65
Unique reflections	2830	11756	4015
Reflections observed [$I > 2\sigma(I)$]	2333	7223	3466
Refined parameters	164	581	190
wR_2 [$I > 2\sigma(I)$]	0.0887	0.0712	0.0608
R_1 [$I > 2\sigma(I)$]	0.0309	0.0292	0.0273
Largest diff. peak and hole peak [e·Å^{-3}]	0.652/ –0.425	0.623/ –0.577	1.625/ –1.156

Conclusion

We investigated the potential of a series of metal halide salts to form highly Lewis acidic compositions in combination with neutral [BMIM][$AlCl_4$] melts. Especially $ZrCl_4$ and $HfCl_4$ readily dissolved in the neutral ionic liquid resulting in Lewis acidic properties comparable to chloroaluminate melts with excess aluminum chloride. The different solubilities of $ZrCl_4$ and $HfCl_4$ in neutral chloroaluminate ionic liquids could provide a new method for the separation of these two metals, which usually display a very similar chemical behaviour.[23] The ternary mixtures catalyzed cationic propene oligomerization reactions, which are typical for acidic binary $AlCl_3$ / BMIMCl mixtures. Crystals of [Ti_2Cl_{10}][BMIM]$_2$, and [Zr_2Cl_{10}][BMIM]$_2$ were obtained from a basic composition, while [Hf_2Cl_9][$PhNMe_3$] crystallized from a neutral [BMIM][$AlCl_4$] melt. The formation of [Hf_2Cl_9]$^-$ anions from such neutral chloroaluminate ionic liquids led to the simultaneous formation of highly Lewis acidic [Al_2Cl_7]$^-$ anions, which were supposed to be responsible for the catalytic activity.

9.3 Experimental Section

All chemical manipulations were carried out using standard Schlenk techniques under argon atmosphere. X-ray crystal structure analyses were performed with a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[24] SHELXL97,[25] and WinGX.[26] Crystallographic details are summarized in **Table 2** and **Table 3**.

Propene (99.3%) was purchased from Riessner Gase, Lichtenfels, and was dried over a column packed with P_4O_{10}. All metal halides were purchased either from ABCR or Sigma-Aldrich and used as received. 1-Butyl-3-methylimidazolium tetrachloroaluminate (BASF), 1-butyl-3-methylimidazolium chloride, and trimethylphenylammonium chloride (Sigma-Aldrich) were used without further purification.

Solubility Determination of $NbCl_5$, $TaCl_5$, $ZrCl_4$, and $HfCl_4$ in [BMIM][$AlCl_4$]

The metal chloride was placed in a Schlenk tube, and one equivalent of [BMIM][$AlCl_4$] was added. The mixture was stirred and heated to 80°C until a homogeneous solution was obtained. If the metal chloride did not dissolve, more ionic liquid was added. Then,

the solution was left standing for two days at ambient temperature. If precipitation occurred, further [BMIM][$AlCl_4$] was added, and the procedure was repeated until a saturated solution of [BMIM][$AlCl_4$] was obtained.

Synthesis of the Ionic Liquid Compositions and Crystallization Experiments

The ionic liquids were synthesized by directly mixing 1-butyl-3-methylimidazolium tetrachloroaluminate with the corresponding metal chlorides. For basic compositions, additional 1-butyl-3-methylimidazolium chloride was added. The trimethylphenyl-ammonium tetrachloroaluminate ionic liquid was obtained by mixing equimolar amounts of $AlCl_3$ and the chloride salt in a cooled Schlenk tube followed by the addition of hafnium tetrachloride. For the crystallization experiments, the compositions were heated to about 60°C and allowed to cool down slowly.

Acknowledgements

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10 Oxidative Coupling and Catalytic Cracking of Alkanes in Lewis Acidic Chloroaluminate Ionic Liquids Enhanced by Molecular Oxygen

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Keywords: chloroaluminates, C-C coupling, ionic liquids, oxygen, cracking

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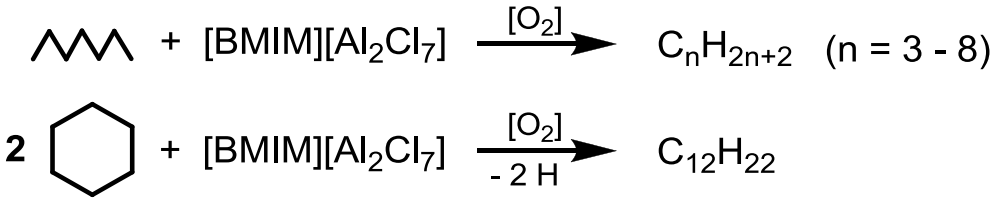
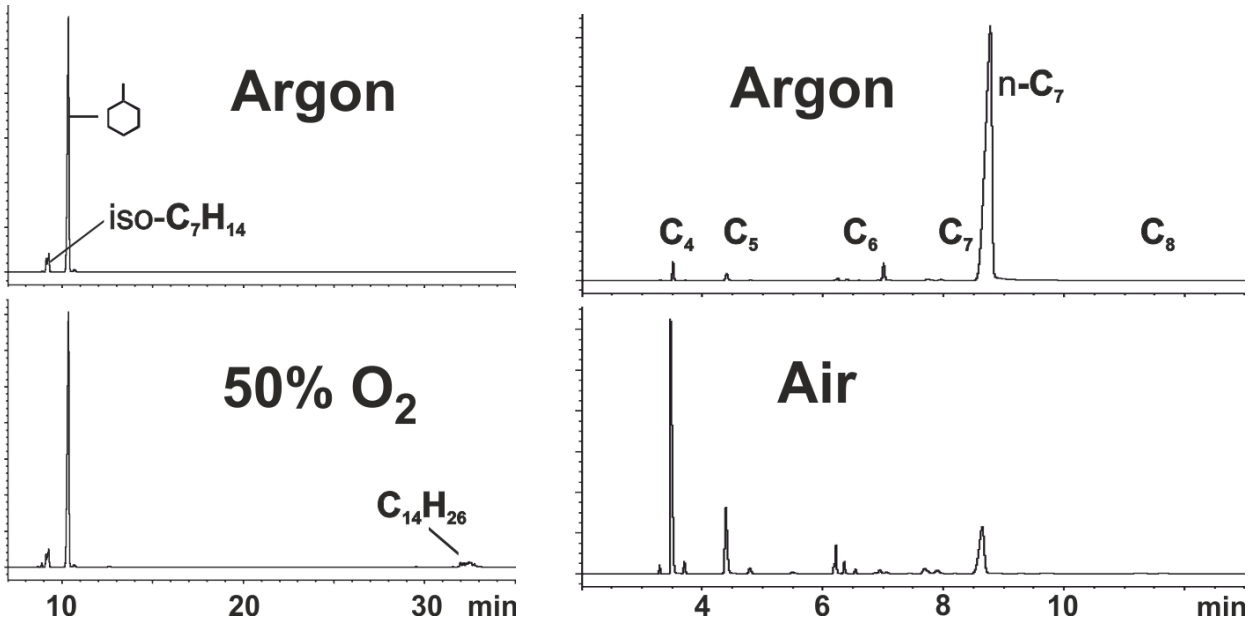


Abstract: In the presence of molecular oxygen, $[BMIM]^+[Al_2Cl_7]^-$ (BMIM = 1-butyl-3-methylimidazolium) ionic liquids catalyzed the oxidative coupling of cyclohexane and methylcyclohexane to give dimers and trimers. Further, conversions and reaction rates of *n*-heptane cracking and disproportionation reactions were strongly enhanced if an atmosphere of dry air was applied instead of an inert gas.

10.1 Main Text

Since the discovery of room temperature chloroaluminate ionic liquids in the 1980s,[1] their Lewis and Brønsted acidic properties were exploited for various biphasic hydrocarbon conversion reactions. Compositions with excess aluminum chloride were found to catalyze cationic olefin oligomerization reactions,[2] isomerization,[3] disproportionation, and cracking[4] reactions of saturated alkanes as well as Friedel Crafts alkylation reactions.[5] Upon addition of excess aluminum chloride to neutral $[cation]^+[AlCl_4]^-$[6] ionic liquids, the formation of highly Lewis acidic $[Al_2Cl_7]^-$ or $[Al_3Cl_{10}]^-$[1a, 6-7] species is responsible for the catalytic activity. Further, traces of water or the addition of hydrochloric acid to chloroaluminate melts generates superacidic protons, which also contribute to the catalytic properties.[8]

Disproportionation and cracking reactions are particularly interesting for hydrocarbon feedstocks, which cannot be used directly. For example, saturated *n*-alkanes containing between five and eight carbon atoms can neither be blended into diesel fuel due to their short chain length nor into gasoline due to their low RONs (research octane numbers).[9]



Scheme 1: GC spectra of the products from biphasic reactions of methylcyclohexane (left) and *n*-heptane (right) with $[BMIM]^+[Al_2Cl_7]^-$ in the presence of argon or molecular oxygen.

Therefore, such paraffins have to be either isomerized to increase their RON[3i] or converted to more valuable hydrocarbons by cracking or disproportionation reactions.[4a] Besides hydrochloric acid, several Brønsted acids and transition metal salt additives were also found to enhance such isomerization reactions.[3a, 3d, 8a] Further, the presence of molecular oxygen was reported to slightly increase the activity of acidic chloroaluminate melts for cationic olefin oligomerization reactions.[10]

We found that the reaction of highly Lewis acidic chloroaluminate ionic liquids with cyclic alkanes led to the formation of oxidative coupling products in the presence of molecular oxygen (**Scheme 1**). Under inert gas conditions, the isomerization of cyclohexane with acidic chloroaluminate melts yielded a thermodynamic equilibrium of cyclohexane and methylcyclopentane.[3f] No cracking or coupling reactions were reported for this system.

Table 1: Oxidative coupling of cyclic alkanes catalyzed by $[BMIM]^+[Al_2Cl_7]^-$ in the presence of molecular oxygen.[1]

No.	Cycloalkane	Gas Phase	Isomers [%][2]	Dimers [%][3]	Trimers [%][3]
1	Cyclohexane	Dry Air	23.8[4]	6.1	0.8
2	Methylcyclohexane	Argon	10.0	0.1	0
3	Methylcyclohexane	Dry Air	11.3	4.4	0
4	Methylcyclohexane	50% O_2[5]	9.2	9.0	0.2

[1] Reaction conditions: 5 ml $[BMIM]^+[Al_2Cl_7]^-$; 150 wt% cycloalkane; T = 100°C; stirring rate = 800 min^{-1}; t = 20 h; 150 ml Schlenk tube. [2] Skeletal isomers. [3] Oxidatively coupled cycloalkane dimers/trimers. [4] Methylcyclopentane. [5] Dry air with additional O_2.

Surprisingly, the same reaction of cyclohexane with $[BMIM]^+[Al_2Cl_7]^-$ at 100°C produced 6.1% $C_{12}H_{22}$ and 0.8% $C_{18}H_{32}$ in an atmosphere of dry air (**Table 1**, experiment 1). The products were identified by GC-MS. With 166 g/mol, the molecular weight of the dimeric coupling product lacked 2 g/mol compared to two cyclohexane molecules. The mass of four hydrogen atoms was missing in case of $C_{18}H_{32}$ compared to three cyclohexane molecules. Therefore, oxidative coupling reactions must have taken place consuming

two hydrogen atoms. For comparison, the reaction was repeated with methylcyclohexane. The reaction in an argon atmosphere yielded 10.0% skeletal isomers from methylcyclohexane and only traces of coupling products (2). While the rate of isomerization remained constant, 4.4% of dimeric coupling products were obtained in an atmosphere of dry air (3) and even 9.0% if the gas phase consisted of 50% molecular oxygen (4). We suppose that oxidative coupling reactions of cyclic alkanes in the presence of molecular oxygen led to the simultaneous formation of water from the abstracted hydrogen atoms. Therefore, reactions in O_2 containing atmospheres should have a similar effect on the reaction performance as the addition of water or hydrochloric acid. In the literature, the positive effect of cyclic hydrocarbon additives on isomerization reactions of paraffins has been described.[3g] Considering our catalytic results, the presence of O_2 impurities in combination with the cyclic hydrocarbon additives might have been responsible for the enhanced reaction rates.

Further, we investigated the effect of molecular oxygen on the reactions of *n*-heptane with $[BMIM]^+[Al_2Cl_7]^-$ (**Table 2**). While only 4% of *n*-heptane reacted to other hydrocarbons in an inert atmosphere (5), 77% of the original amount of *n*-heptane was converted to hydrocarbons with higher or lower carbon numbers in an atmosphere of dry air (6).

Table 2: Cracking reactions of *n*-heptane catalyzed by $[BMIM]^+[Al_2Cl_7]^-$ in the presence of molecular oxygen.[1]

No.	Gas Phase	Conversion[2] [%]	*i*-C_7 [%]	C_3 [%]	C_4 [%]	C_5 [%]	C_6 [%]	> C_7 [%]
5	Argon	3.6	< 0.1	< 0.1	1.4	0.9	0.5	0.7
6	Dry Air	76.6	4.0	0.9	42.7[3]	15.6[4]	8.6	4.8

[1] Reaction conditions: 5 ml $[BMIM]^+[Al_2Cl_7]^-$; 150 wt% *n*-heptane; T = 100°C; stirring rate = 800 min^{-1}; t = 20 h; 300 ml glass autoclave. [2] Sum of all disproportionation, cracking and isomerization products. [3] 40.9% isobutane, 1.8% *n*-butane. [4] 14.3% 2-methylbutane, 1.3% *n*-pentane.

The main products were identified as butanes (43%), pentanes (16%), and hexanes (9%) by direct gas chromatographic analysis of the liquid nitrogen cooled product phase (**Scheme 1**). The oxygen free system displayed only a minor isomerization activity and

produced higher hydrocarbons compared to the O_2 containing system. This effect matched to the observation that oxygen containing systems turned dark brown during the reaction. We assume this might be derived from coking effects since carbon rich products must be obtained parallel to the formation of short chain alkanes. No colour changes were observed for the ionic liquids used under inert conditions.

Upon contact with 15 wt% shreds of an unprinted commercial LDPE plastic bag under the same conditions applied for *n*-heptane, the polyethylene was cracked to yield about 8% propane, 75% butanes, 14% pentanes, and 3% hexanes in the gas phase. No solid insoluble polymer was left after the reaction.

We have shown that molecular oxygen strongly enhanced the conversions and reaction rates in biphasic cracking reactions of paraffins. Further, the combination of highly Lewis acidic chloroaluminate ionic liquids with O_2 catalyzed oxidative coupling reactions of cyclic alkanes, which have not been reported yet. The presence of dry air in such biphasic hydrocarbon conversion reactions provides a promising alternative to Brønsted acid or transition metal additives applied with Lewis acidic chloroaluminate melts. Reactions in air facilitate the handling and thus, drastically improve the process economics for large scale applications.

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11 List of Publications

The following manuscripts were written during the work on this thesis and will be submitted as soon as our cooperation partner, ConocoPhillips, approved the publication in scientific journals:

1. M. Dötterl, H. G. Alt; *to be submitted*

   “Heavy Metal with Heavy Impact: Olefin Dimerization Reactions in Triphenylbismuth Buffered Chloroaluminate Ionic Liquids”

2. M. Dötterl, P. Thoma, H. G. Alt; *to be submitted*

   “Facile Synthesis of new Cationic Triphenylphosphine Derivatives and their Use for Propene Dimerization Reactions in Buffered Chloroaluminate Ionic Liquids”

3. M. Dötterl, H. G. Alt; *to be submitted*

   “Nickel Catalyzed Propene Dimerization Reactions in $BiPh_3$ Buffered Chloroaluminate Ionic Liquids: High Performance with Unconventional Cations”

4. M. Dötterl, H. G. Alt; *to be submitted*

   “Buffered Aluminum Chloride as Highly Efficient Cocatalyst for Olefin Dimerization and Polymerization Reactions”

5. M. Dötterl, H. G. Alt; *to be submitted*

   “Silica Supported Cocatalysts for Olefin Dimerization and Polymerization Reactions with Nickel Complexes”

6. M. Dötterl, I. Haas, H. G. Alt; *to be submitted*

   “Solubility Behaviour of $TiCl_4$, $ZrCl_4$, and $HfCl_4$ in Chloroaluminate Ionic Liquids”

7. M. Dötterl, H. G. Alt; *to be submitted*

   “Oxidative Coupling and Catalytic Cracking of Alkanes in Lewis Acidic Chloroaluminate Ionic Liquids Enhanced by Molecular Oxygen”

List of Patents and Patent Applications

During the work on this thesis the following invention records, patents, and patent applications were elaborated:

No.[1]	Inventors[2]	Title	Status[3]	Date
IR-41028	TE, CD, MD, HA, RS	Selective Olefin Dimerization with Supported Metal Complexes Activated by Alkylaluminum Compounds or Ionic Liquids	Filed	07/2009
IR-41029	TE, CD, MD, HA, RS	Organometallic Complexes as Catalyst Precursors for Homogeneous Dimerization Reactions of 1-Olefins	Filed	07/2009
IR-41190	MD, HA, RS	Buffered Ionic Liquids for Selective Olefin Dimerization	Filed	03/2010
IR-41270	MD, HA, RS	Method for Supporting homogeneous Catalysts	Filed	07/2010
IR-41363	MD, HA, RS	Highly Active and Selective Dimerization of Internal Olefins with Highly Lewis Acidic Guanidinium Based Chloroaluminate Ionic Liquids	Approved	10/2010
IR-41482	MD, HA, RS	Enhanced Alkane Isomerization by Precious Metal Containing Chloroaluminate Ionic Liquids	Approved	10/2010
IR-41578	MD, HA, RS	$AlCl_3$ Based Cocatalysts	Submitted	08/2010
IR-41579	MD, HA, RS	Buffered Ionic Liquids for Selective Olefin Dimerization (Update)	Submitted	08/2010
IR-41580	MD, HA, RS	Polymerization in Buffered Chloroaluminate Ionic Liquids	Submitted	08/2010
IR-41610	MD, HA, RS	Heterogeneous Silica Based Cocatalysts for Nickel Catalyzed Dimerization and Polymerization Reactions of Olefins	Submitted	08/2010
IR-41614	MD, HA, RS	Oxidative Coupling of Cyclic Alkanes and Catalytic Cracking of *n*-Alkanes in Chloroaluminate Ionic Liquids Enhanced by Molecular Oxygen	Submitted	09/2010

[1] Internal ConocoPhillips registration code. [2] MD = Matthias Dötterl; HA = Prof. Dr. Helmut G. Alt; RS = Dr. Roland Schmidt (ConocoPhillips representative); TE = Tanja Englmann, CD = Dr. Christine Denner. [3] Filed = Patent/Application was filed at the US patent office; Submitted = Invention record was submitted to the ConocoPhillips patent division and is under investigation; Approved = Patent/Application was approved by ConocoPhillips for filing at the US patent office.

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13 Declaration / Erklärung

I hereby declare that I have written this work by myself and that no other sources than those mentioned in this work have been used.

This work has so far neither been submitted to the Faculty of Biology, Chemistry and Earth Sciences at the University of Bayreuth nor to any other scientific institution for the purpose of a doctoral thesis.

Hiermit versichere ich an Eides statt, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel und Quellen angefertigt habe.

Diese Arbeit wurde bisher weder an der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht.

Matthias Dötterl